Bipolar Electrochemistry for high throughput screening applications

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**Abstract**


Bipolar electrochemistry is an interesting concept for high throughput screening techniques due to the ability to induce gradients in a range of materials and their properties, such as composition, particle size, or dopant levels, among many others. One of the key advantages of the method is the ability to test, create or modify materials without the need for a direct electrical connection. In this thesis, the viability of this method has been explored for a range of possible applications, such as metal recycling, nanoparticle modification and corrosion analysis.

In the initial part of the work a process to electrodeposit gradients in metal composition was evaluated, with a view to applying the technique to the extraction and recycling of metals from fly ash. Compositional gradients in the metals under study could be readily obtained from controlled reference solutions, although the spatial resolution of the metals was not sufficient to perform separation. Only copper could be easily deposited from the fly ash solution.

Bipolar electrodeposition was also successfully used to modify the particle size across substrates decorated with gold nanoparticles. The approach was demonstrated both for surfaces possessing either a uniform particle density or a gradient in particle density. In the latter case samples with simultaneous, orthogonal gradients in both particle size and density were obtained.

A combination of the bipolar approach with rapid image analysis was also evaluated as a method for corrosion screening, using quantitative analysis of gradients in pitting corrosion damage on stainless steels in HCl as a model system. The factors affecting gradient formation and the initiation of corrosion were thoroughly investigated by the use of a scanning droplet cell (SDC) technique and hard x-ray photoelectron spectroscopy (HAXPES). The ability to screen arrays of different materials for corrosion properties was also investigated, and demonstrated for stainless steel and Ti-Al alloys with pre-formed compositional gradients. The technique shows much promise for further studies and for high throughput corrosion screening applications.

**Keywords:** bipolar electrochemistry, electrodeposition, corrosion, screening, gradients, recycling, gold nanoparticles, Scanning Droplet Cell, Hard x-ray photoelectron spectroscopy, pitting corrosion

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urn:nbn:se:uu:diva-277937 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-277937)
Till min familj,
Det kan aldrig ta slut.
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  S. Munktell, M. Hahlin, F. Björefors, Bipolar electrodeposition of heavy metal compositional gradients. Manuscript


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Contributions to the papers

Paper I. Planned the experiments, executed all the experimental work, performed the analysis. Major contributor to the writing of the manuscript. Main author.

Paper II. Performed the data evaluation and calculations, participated in the discussions of the results. Co-author and proof reader of the article.

Paper III. Took part in the experimental work and analysis of the samples, participated in discussions of the results. Major contributor to the writing of the manuscript. Main author.

Paper IV. Planned the experiments, took a major part in the experimental work and evaluation of the results. Major contributor to the writing of the manuscript. Main author.

Paper V. Planned the experiments, performed all the experiments and data analysis. Major contributor to the writing of the manuscript. Main author.
1. Introduction

What first comes to mind at the mention of the word bipolar might not be connected to chemistry or natural science at all. The basic definition is that something exhibits two opposite extremes, much like the carnation in Figure 1. In bipolar electrochemistry it implies that an object acts simultaneously as an anode and a cathode (the positive pole and the negative pole respectively in an electrolytic cell). How does this occur, and what implications does it have? To answer the first question we can consider the following metaphor.

Picture a pedestrian crossing with a mass of people struggling to cross a busy street. The traffic is heavy and the crowd is moving slowly. This problem can be solved by the construction of a bypass in the form of a bridge or a tunnel that provides an alternative route for the people. The number of people who will take the bypass route will depend on a variety of factors that, simply speaking, constitute the path of least resistance. A bipolar electrode works by the same principle, but instead of people there is a flow of charge. Here, instead of the road, there is an electrolyte through which the electrons must pass, and instead of the bypass there is the bipolar electrode. Similes can be drawn between the different factors that compel people to choose either the normal crossing or the bypass, and why the flow of charge may take an alternative path.

When an electric field is applied across an electrolyte containing conducting objects, these conductors can become bipolar. If the potential difference across the object, or objects, is high enough, part of the total cell current can pass through this alternative route via electrochemical reactions, as a gradient from oxidation to reduction, taking place on the surface of the object. In this way, a potential gradient across the now bipolar electrode is introduced by the external field.
A straightforward experiment that illustrates the bipolar effect in an electrochemical cell is to place a platinum foil in an electrolyte composed of water and a universal pH-indicator, and apply an external potential difference across it, as shown in Figure 2. Water oxidation and reduction will take place on the two poles of the platinum foil surface when the potential is sufficient to drive these reactions. This in turn will generate local changes in pH close to the poles of the sample, subsequently causing a change in colour due to the indicator.

Figure 2. A bipolar system, formed from a platinum foil submerged in a solution of universal indicator and water. The bipolar effect is generated by the application of 10 V between the two feeder electrodes.

In nature, bipolar electrodes can occur unintentionally causing a phenomenon commonly known as stray current corrosion, when, for example, a current coming from an outer source such as a railroad can take an alternative path through an underlying pipe. While this can be disastrous, the bipolar effect has also proved to have many beneficial applications in a wide range of fields, which vary from large scale industrial reactors to sensors and analytical methods, to shaping nano-sized objects. Major advantages with the technique are the ability to form different types of gradients, and application to arrays of samples for screening. The fact that no direct electrical contact is necessary makes it simpler to apply to objects that otherwise might have been difficult to connect to a circuit.

The scope of this work has been to study both poles of the bipolar electrode for alternative ways of using the unique capability of bipolar electrochemistry to create gradients in materials. The targeted applications cover both anodic and cathodic processes; from corrosion of steel to electrodeposition. The aim of this thesis, therefore, is to explore and develop new methods of using bipolar electrochemistry as a tool for screening of material properties and to modify surfaces. A consequential aim from this is to deepen our knowledge about bipolar electrochemistry as a whole.
2. Background/Theory

2.1 Bipolar electrochemistry

Bipolar electrochemistry can seem, and often is, quite simple to set up experimentally, however there are many factors to consider to create a controlled system. The unique properties of a bipolar electrode arise from the fact that its polarisation is controlled externally and indirectly via the gradient in the solution potential. This contrasts with the common electrochemical setup where all electrodes are in electrical contact to the power source.

The bipolar electrode is generated by the application of a potential difference across two feeder electrodes, creating a gradient in the solution potential. This subsequently creates a gradient in the potential difference between the solution and the surface of a conducting object in the solution, along the entire length of that object. When this potential difference is sufficient, electrochemical reactions can take place, with oxidation reactions occurring at the end of the object facing the negative feeder electrode (the anodic pole of the now active bipolar electrode), and *vice versa* for the reduction. Part of the total cell current \( i_{\text{tot}} \) now passes through the bipolar electrode \( i_{\text{bpe}} \), with the remaining current passing through the electrolyte \( i_{\text{electrolyte}} \). Without the bipolar electrode, \( i_{\text{tot}} = i_{\text{electrolyte}} \), when including the bipolar route the equation becomes \( i_{\text{tot}} = i_{\text{electrolyte}} + i_{\text{bpe}} \). This is shown schematically in Figure 3.

![Figure 3. Schematic of the bipolar system. E indicates the direction of the applied external electric field.](image)

\[ i_{\text{tot}} \] \[ i_{\text{electrolyte}} \] \[ i_{\text{bpe}} \] \[ \text{Power source} \] \[ \text{Feeder electrode} \] \[ \text{Bipolar electrode} \] \[ \text{Feeder electrode} \] \[ \text{Reduction} \] \[ \text{Oxidation} \] \[ E \] \[ i_{\text{bpe}} \] \[ i_{\text{electrolyte}} \]
The floating potential of the bipolar electrode, because of the lack of external connection, makes it difficult to determine the exact potential difference at a given point on the surface of the electrode. This is also one of the inherent challenges with the technique. A conventional method of determining the theoretical maximum potential difference across a bipolar electrode, $\Delta E_{BPE}$, generally follows Equation 1:

$$\Delta E_{BPE} = E_{tot} \left( \frac{l_{BPE}}{l_{channel}} \right)$$

Where $E_{tot}$ is the applied external potential, $l_{BPE}$ is the length of the bipolar electrode and $l_{channel}$ is the distance between the feeder electrodes. From this equation, it is seen that a longer object, relative to the length of the channel, will become bipolar at lower external field strengths, and that a much stronger field, of magnitudes of up to 1000 kV/m\(^{14}\), is needed for small objects such as nano-particles. The external field strength is also directly related to the conductivity of the electrolyte. Thus, the composition of the electrolyte is a very important factor: if its conductivity is too high, the potential drop across the object will not be sufficient to drive reactions on the bipolar electrode surface, and the current will pass through the electrolyte only. This also implies that the conductivity of the would-be bipolar electrode is important, as well as how easily reactions can occur on its surface.

Similarly, because of the lack of external connection, $i_{bpe}$ cannot be determined directly in this basic setup. Moreover, the current density at any given point on the surface is even more difficult to determine. The gradient in electrochemical potential on the electrode means there is a corresponding gradient in the overpotential for electrochemical reactions taking place on the surface. There is therefore a gradient in the current density profile across the electrode.

Duval et al.\(^{15-17}\) demonstrated how the current density along a bipolar electrode could be modelled by studying dissolution of aluminium wafers acting as bipolar electrodes. The model is based on some general assumptions such as electric field homogeneity and irreversible electrontransfer-limited reactions. Thus, the model tells only a part of the whole story, however it still provides a simple and illustrative way to appreciate the faradaic current profile across the surface. Effects of changing system parameters such as the feeder field strength or electrode sizes can also be evaluated using this model. Mavré et al.\(^{3,18}\) later undertook similar studies based on measuring the electrogenerated chemiluminescence of ruthenium complexes at bipolar electrodes. A schematic illustration of their validated model is presented in Figure 4.
Figure 4a and b, illustrates how the fraction of the current passing through the bipolar electrode depends on relative values of the resistance of the electrolyte ($R_e$) and of the total resistances related to the bipolar electrode ($R_{bpe}$). The change in potential drop and local decrease in electric field close to the bipolar electrode, induced by part of the total current flowing through the bipolar electrode is shown in Figure 4c and d, respectively. Finally Figure 4e, depicts the current profile across the bipolar electrode.

The bipolar electrode itself accumulates no net charge, which means that the reactions taking place on the two poles have to balance and the rate of oxidation and reduction must be equal. As a result one process will limit the current through the bipolar electrode. A simple method to extract the bipolar current is to use split bipolar electrochemistry$^{19,20}$. In this type of setup, the
two poles of the electrode are separated and an ammeter monitoring the current connects them instead.

Ulrich et al.\textsuperscript{21,22} further visualised the current and potential profile across bipolar electrodes using imaging surface plasmon resonance (iSPR) and correlated these results with simulations of the system. The purpose of the study was to determine how to better employ bipolar electrochemistry for the formation of surface gradients. The group also found that standard Ag/AgCl reference electrodes, when connected to the bipolar electrode and positioned precisely above the surface at desired locations, could be used to estimate the potential differences along the gradient. The requirement of a direct connection to the bipolar electrode in the experiment performed by Ulrich et al., removes one of the main advantages of this system. However, a reference used in this way can partly circumvent the difficulties in determining the exact conditions along a bipolar electrode. Ulrich et al. furthermore demonstrated that two movable reference electrodes, held at a constant distance from each other, could be used to determine the relative iR-drop at different points above a bipolar electrode, without requiring direct electrical contact.

The early applications of bipolar electrochemistry were already established by the time the studies described above were performed. With these insights a rational design approach has, and continues to be, implemented to develop sophisticated new strategies within the field of bipolar electrochemistry.

2.1.1 Background to bipolar electrochemistry

Apart from a recent re-birth of research into the system during the last two decades, the modern history of bipolar electrochemistry began in the early 1970s with the design and study of different types of electrochemical reactors\textsuperscript{1,12}. Promising features such as fewer external connections and the possibility to have large active surface areas gave rise to a number of new concepts in industry and research. Today, many large scale applications are still based on bipolar electrochemistry, across such different areas as batteries, fluidized bed reactors and methods for steel treatments\textsuperscript{23,24}. In the steel manufacturing industry, electrolytic pickling is a known method to modify the protective oxide layer of steel\textsuperscript{25–29}. In this process, steel sheets pass between two outer feeder electrodes causing the sheets to act as bipolar electrodes, where one side oxidises to form a thicker passive layer.

For battery applications it has been shown that stacks of bipolar electrodes can be used to minimize Ohmic resistances and optimise the surface area in contact with the electrolyte\textsuperscript{30}. The concept has been adapted to many of the commercial technologies such as nickel-metal hydride, Li-ion systems\textsuperscript{31} as
well as the old classic, lead-acid. A schematic of a stacked bipolar system is seen in Figure 5a.

In other fields, stacked bipolar electrodes are commonly used for electrowinning, different kinds of electrosynthesis\textsuperscript{32}, and water cleaning\textsuperscript{33}. The stacks are adapted to their purpose and vary from simple metal plates to complex types of particle beds. If, instead of fixed bipolar structures, the system consists of particles that are dispersed in a flowing electrolyte, the system is known as a fluidized bed electrochemical reactor. These types of reactors have been extensively studied and it has been suggested and experimentally verified that their effectiveness is a result of the particles acting as individual bipolar electrodes. The technique is suitable for applications such as copperwinning and water splitting, among others\textsuperscript{34}. Apart from the general advantages with the bipolar approach described earlier, these types of reactors can have self-cleaning properties. That is, since the particles move freely in the solutions, they can rotate and therefore change polarity, which enables the removal of residues that may have formed on the surface. Figure 5b, depicts a schematic of a fluidized bed reactor.

Figure 5. a) Schematic of a stacked bipolar electrode, b) Schematic of a fluidized bed reactor.

Aside from the large scale industrial applications, bipolar electrochemistry creates a multitude of promising research opportunities. The ability to asymmetrically alter objects, to create gradients in materials and the potential for wireless setups are all reasons to study the phenomenon further\textsuperscript{35–37}. Kuhn’s group at the University of Bordeaux have focused much of their work on the generation of different types of asymmetrically modified particles (Janus particles)\textsuperscript{14,35,38–44}. During the last decade they have introduced a
The bipolar effect has also been widely applied in different types of sensor systems\textsuperscript{3,5,7,18,45,46}. As described previously, there does not necessarily have to be a single bipolar electrode in solution. If there are a multitude of objects in the electrolyte they can all act as individual bipolar electrodes. This behaviour has proved to be very useful, and there are numerous applications that take advantage of it. For example, a common approach is to create arrays of samples that individually act as bipolar electrodes to build wireless DNA-sensors or facilitate catalyst screening\textsuperscript{36}. Since no external wires are needed, these setups can be simple and straightforward.

A common theme in all of the above examples is that in each case there are objects with two sides exhibiting completely different properties, that is, they have both a cathodic and anodic pole. However, many applications tend
to focus on only one half of the bipolar electrode. The cathodic end of a bipolar electrode, for example, can be exploited for electrodeposition of various materials and the formation of compositional gradients within them. Materials with a more negative reduction potential will deposit nearer the cathodic edge of the electrode, where the polarisation is greatest. An illustrative example of this was shown by Ramakrishnan et al. who reported the formation of gradients in sulphur and cadmium on a gold bipolar electrode. The compositional gradient ranged from elemental sulphur near the middle, to semiconductor CdS, and pure Cd at the cathodic edge. The same group also presented a concept to deposit and screen the optical properties of Ag-Au alloy gradients by bipolar electrochemistry. Moreover, in recent years, a range of different techniques utilising bipolar electrodeposition have been suggested. For example, studies of the voltammetric response and electron transfer reactions of bipolar cells for electroless deposition of copper. Some other applications include controlled growth of contacts between particles to create electrical circuits and asymmetric modification of carbon nanotubes. More recently, Sopha et al. introduced a concept of wireless electrosampling of heavy metals on glassy carbon beads acting as bipolar electrodes. Kayran et al demonstrated how a bipolar electrodeposition approach could be employed to find the optimal conditions for deposition of gold substrates for surface-enhanced Raman scattering (SERS).

At the anodic pole, on the other hand, oxidation reactions take place. Thus, the potential applications of this pole are fundamentally different from those involving the cathodic pole. Inagi’s group established an approach to employ the anodic pole to perform gradual electrochemical doping of conducting polymers. Other reported applications include physico-chemical milling of metal beads and controlled anodisation of TiO₂ nanotube gradients. The anodic dissolution of chromium was utilised to evaluate the effectiveness of catalysts for hydrogen production in array setups. Catalyst particles were connected with ribbons of chromium, forming the cathodic and anodic parts respectively on each bipolar object in the array. A more effective catalyst has a lower resistance to hydrogen evolution, resulting in a higher current density on that particle. The quantity of chromium dissolved from the anodic part of the object will be proportional to the catalytic current, and therefore provides a quantitative measure of catalyst activity.

As shown above, the applications utilising the unique properties of bipolar electrodes are plenty. Nevertheless, there are still many unexplored possibilities to employ this versatile technique.
2.2 Potential applications

In this work, bipolar electrochemistry was evaluated for new applications within the field of corrosion analysis and some aspects of electrodeposition of gradients. The following section will therefore provide a brief introduction and background to these two fields.

2.2.1 Electrodeposition

Electrodeposition is a general term for different systems that utilise electrochemical processes to deposit material on a surface. This approach has been widely used to generate coatings for decorative purposes and corrosion protection, among many other applications. Gradients in electrodeposited materials can be readily generated by bipolar electrochemistry due to the variable driving force for reduction or oxidation along the bipolar electrode. The gradients that can be created by bipolar electrodeposition can be in a range of different properties, such as size, shape or composition, as outlined in the previous section. A number of potential applications for gradients in electrodeposited materials have been covered in a recent review.

Two methods for performing bipolar electrodeposition are presented in this thesis. The first is an approach for studying how different heavy metals electrodeposit on a bipolar electrode, with the purpose of evaluating screening and recycling possibilities. The second application utilises the bipolar effect to modify the size of gold nanoparticles distributed on a planar surface.

One of the industrial applications of bipolar electrodes is the recovery of copper from wastewater for recycling. Copper is one of the few metals which can be isolated from mixtures of other metals electrochemically because of its relatively high reduction potential. This is commonly done industrially through the use of fluidized-bed reactors as described in Section 2.1.1.

Another example of a recycling procedure to which electrodeposition is relevant is the treatment of fly ash. Fly ash is residual ash that is collected in smoke from the incineration of waste. It contains large fractions of heavy metals, including around 800-900 mg of copper and 250-300 mg of lead per kilo, and so is classified as hazardous waste which makes it difficult to store or deposit. Ideally, the metals in the ash can be extracted and recycled, and the remaining non-hazardous ash can be deposited safely. The complex composition of the ash, however, causes problems in the development of effective recycling strategies. To screen solutions of dissolved ashes for their different metal components and to study how they can be recovered electrochemically would therefore be of great relevance. The gradient in reduction
potential along the cathodic edge of a bipolar electrode could provide a possible route to this. In principle, metals would deposit at different positions along a large, planar bipolar electrode according to their individual reduction potentials. If the metals can be separated sufficiently this approach would be considerably simpler and quicker than existing methods.

It has previously been demonstrated that gold nanoparticles can be irreversibly chemisorbed on dithiol-modified gold surfaces for cell screening\textsuperscript{72,73}. The number of particles on the surface can be fine-tuned either to form a specific particle distribution over the entire surface, or to generate gradients in the particle distribution. Nanoparticle-coated surfaces have been used to study different biological systems such as cell adhesion\textsuperscript{74} or for insulin sensors\textsuperscript{75}. Adding another dimension to these surfaces could increase their potential range of applications. For example, bipolar electrodeposition provides the possibility for introducing a gradient in particle size across gold nanoparticle modified surfaces.

2.2.2 Corrosion

Corrosion is a collective name for degeneration of a material via reactions with its surrounding environment. While most commonly associated with rust that is the oxidation of iron, most materials corrode in one way or another. For this reason corrosion can have catastrophic consequences when it occurs in the wrong places. Worldwide, corrosion is very costly, can cause the spreading of hazardous compounds and increases the strain on the supply of natural resources. Therefore, it is of utmost importance to study the corrosion properties of materials, learn how to predict a materials behaviour, prevent damage, suitably protect them and choose the right material for the right application. While there are various kinds of corrosion\textsuperscript{76}, those addressed in this thesis are uniform/general corrosion and pitting corrosion. Uniform corrosion is simply the homogeneous oxidation of a surface. Pitting corrosion, however, is a type of local corrosion that predominantly occurs on materials that have a passive film of some form\textsuperscript{77}.

The passive film on stainless steel

The resistance of a material to corrosion depends heavily on its surface structure. Many metals and alloys naturally form a passivating film in contact with different environments. The properties of the film will depend on the composition of the material and its surroundings, and a stable surface layer can protect the material from degradation\textsuperscript{78,79}. A well-known group of materials whose performance is determined by their passive film are stainless steels. These thin passive films, typically 1 – 3 nm thick, mainly consist of oxides and hydroxides of the metals in the steel\textsuperscript{79,80}.
The susceptibility of a stainless steel to pitting corrosion is predominantly determined by the passive film. An indication of the resistance of a steel to pitting corrosion can be provided by calculating its Pitting Resistance Equivalent Number (PREN), which is determined by the alloy composition according to Equation 2:

\[
PREN = \%Cr + (3.3 \times \%Mo) + (16 \times \%N)
\]

A schematic of the surface layers formed in acidic conditions on a standard stainless steel is seen in Figure 7. At the outermost layer, chromium hydroxide is more pronounced, while further down chromium oxide is a dominating component of the film. This is partly caused by selective dissolution of iron oxides/hydroxides near the surface leaving a chromium-enriched film. Nickel enrichment just below the passive film is also known to occur on some steels.

Figure 7. Schematic of the passive film on stainless steel.

**Pitting corrosion**

The passive film typically protects the underlying material, however, this very aspect of the film can lead to pitting corrosion. Pits often form in salt-containing solutions, where anions such as halides weaken the passive film by penetrating it and exchanging with oxide anions to then form soluble species. Generally, this occurs where the film is weaker, because of damage or a natural defect, such as at a grain boundary. When the passive film is broken, the underlying surface is unprotected and the corrosion rate is accelerated within this area, causing the pit to grow. Damage caused by pitting corrosion can be very insidious as it is difficult to assess its extent; a pit can look like a small spot while the actual damage proceeds deep down underneath the surface, as shown in Figure 8a and b. This factor can also make pitting corrosion problematic to study using conventional methods.
Stray current corrosion (SCC)

Corrosion, such as the uniform and pitting variants discussed so far, can arise spontaneously, as electron transfer can be facilitated by natural sources, such as dissolved oxygen. However, corrosion can also be caused unintentionally and unintentionally. Such a form of corrosion, directly connected to bipolar electrochemistry, is known as stray current corrosion, or leakage current corrosion. This type of corrosion occurs when bipolar electrodes arise because of proximity to external electrical currents. The effect can cause severe damage in, for example, environments with power lines that can leak current to underlying pipes. This process is schematically depicted in Figure 8c. In this example, a direct current is used to drive a train. The main current path, thus, flows through the train and track. However, if there is an alternative path, such as an underlying pipeline, and the soil can act as electrolyte, part of the current can instead pass through the pipe. This results in corrosion at the part of the pipe acting as the anode where the electrons are exiting the surface. In some cases SCC can cause significant damage within days or even hours. Figure 8d, shows a shaft that has been subject to stray current corrosion. Interestingly, it has been suggested that SCC can be utilised to
construct probes for contactless evaluation of the corrosion properties of reinforced steel in cement and concrete\textsuperscript{86,87}. The technique involves the application of an outer field to a reinforced block, and utilises changes in conductivity brought on by the bars acting as bipolar electrodes to predict how they will corrode. This contactless approach contrasts with many common methods for analysing corrosion properties, which require direct contact to the material in question.

**Corrosion analysis**

To study and evaluate the corrosion properties of materials is of great importance. Standard systems for corrosion analysis commonly involve electrochemical characterisation techniques such as polarisation methods or impedance spectroscopy\textsuperscript{88,89}, in addition to approaches like exposing the materials to different environments and waiting to see how they react\textsuperscript{85,90–92}. There are also many combinatorial approaches utilising local probe techniques or refined array systems\textsuperscript{92–95}. What many of these tests have in common is that they are time-consuming and some of them require advanced evaluation of the result. Thus, a method that can, in a short amount of time, provide easily comprehensible evaluation of the corrosion properties of materials would be very valuable.

Bipolar electrochemistry presents an opportunity to provide a streamlined method for corrosion screening. Ideally, the gradient in oxidation reactions across the anodic pole of the bipolar electrode can be used to induce a gradient in corrosion damage along a surface. In this way, different stages of corrosion can be evaluated on the same sample in a single experiment. There is also the prospect of increasing the throughput of the approach by placing a number of samples in the same setup and exposing them simultaneously to an external field.
2.3 Scope of the thesis

The scope of this work has been to study and present new possible applications for bipolar electrochemistry. The studies are divided into cathodic and anodic applications, depending on which of the two poles of the bipolar electrode that was in focus. A general aim of the work was also to increase the overall knowledge of how and what influences a bipolar electrode. Broadly, the aims of this thesis are to:

**Cathode**

- Explore the possibility to form compositional gradients by co-deposition of different metals using bipolar electrodeposition. Evaluate if this approach can be used to screen solutions containing dissolved fly ash for possible recycling opportunities.
- Perform bipolar electrodeposition of gold onto substrates covered with gold nanoparticles in order to generate gradients in particle size.

**Anode**

- Introduce the concept of bipolar electrochemistry for the screening of corrosion properties materials.
- Perform in-depth analysis of how a steel sample exposed to different bipolar experimental conditions is influenced.
- Evaluate if, and how, the throughput of the bipolar corrosion screening can be increased by studying arrays of steel samples.
- Test if samples with a compositional gradient can be screened by generating two-dimensional corrosion gradients.
3. Methodology

In this chapter the methods, materials and experimental setups described in this thesis are summarised. A short description of the different analytical techniques applied in the studies is also provided.

3.1 Substrates

Gold substrates
Silicon wafers coated with a 200 nm thick layer of gold were employed as a standard substrate for the metal gradient experiments in paper I. The wafers were pre-cut to a standard size of 20 x 10 mm².

Gold nanoparticle substrates
The gold nanoparticle substrates used in paper II were prepared by chemisorption of 10 nm particles onto planar, thiolated gold surfaces with a size of 10 x 11 mm². The particles carry a sufficient zeta potential which allows them to spontaneously self-organise on the surface, because of mutual electrostatic repulsion. The distance between particles and number of particles per area can be tuned by altering the ionic strength. Particle density of the substrates was defined as the part of the surface covered by particles. Gradients in particle density can be generated across the surface by injecting a relatively concentrated salt solution into the bottom of the container containing the nanoparticle solution, and immersing the substrate while the salt ions diffuse. The gradient in particle density reflects the gradient in the ionic strength of the solution. Two types of substrates, one with a particle density of 10 %, and a gradient, were studied in the experiments. A setup consisting of two Pt-feeder electrodes separated by 4 cm in a plastic petri dish was employed to perform the bipolar electrodeposition. The electrolyte consisted of 8 mM NaCl, 5 mM sodium citrate and 2 mM HAuCl₄.

Steel samples
Five different grades of steel have been studied in this work. The 304 grade was initially used to demonstrate the generation of corrosion gradients, and to study gradient formation. This work is presented in papers III and IV. The four other grades were added, to the sample matrix for the array experi-
ments in paper V. Their respective compositions and PRE-numbers are given in Table 1. To provide comparable results, all steel samples were ground and polished in the same way and then allowed to rest in ambient conditions to form a new native oxide layer.

Table 1. Steel grade compositions and PRE-number for five steel grades investigated in this work.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Alloying elements in weight-%</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>0.015 C, 18.15 Cr, 8.44 Ni, 0.41 Mo, 0.35 Si, 1.74 Mn, 0.031 P, 0.01 S, 8.44 Ni, 0.069 N, 0.25 Cu, 0.001 Ti, 0.002 Ce</td>
<td>21</td>
</tr>
<tr>
<td>2205</td>
<td>0.02 C, 22 Cr, 5.7 Ni, 3.1 Mo, 0.17 N</td>
<td>35</td>
</tr>
<tr>
<td>MV</td>
<td>0.05 C, 18.2 Cr, 9 Ni</td>
<td>18</td>
</tr>
<tr>
<td>SK</td>
<td>0.05 C, 17 Cr, 10.9 Ni, 2.7 Mo</td>
<td>26</td>
</tr>
<tr>
<td>SL</td>
<td>0.05 C, 16.7 Cr, 15.9 Ni, 4.2 Mo</td>
<td>31</td>
</tr>
</tbody>
</table>

**TiAl-alloys**

In the last part of the work a concept to screen thin films with compositional gradients was tested. TiAl films with continuous compositional gradients were deposited in a custom-built multi-gun magnetron sputtering system, at room temperature. The gradient across the sample ranged from 64 % Al and 36 % Ti (“Al-rich”) to 39 % Al and 61 % Ti (“Ti-rich”).

### 3.2 Bipolar electrochemistry experiments

**Bipolar electrodeposition**

Exploitation of the possibilities of bipolar electrodeposition of metals was undertaken using a setup consisting of a 20 x 30 mm Teflon cell, platinum feeder electrodes and an Ivium Compactstat as the power source. The different electrolytes were prepared as to have similar properties with regard to conductivity and pH.

**Bipolar corrosion experiments**

The initial corrosion experiments were performed using a round glass cell, with a diameter of 50 mm. The anodic feeder electrode was platinum foil and the cathodic electrode was stainless steel. This setup was employed to test settings and establish which types of electrolytes were suitable for the system. Subsequently two new cells, made from Teflon were implemented to provide a consistent setup with a fixed size. The different systems are described further in the respective papers *i.e.* paper III-V. For the corrosion
evaluation of sputtered TiAl-alloy gradients, a 50 x 50 mm Teflon vessel was used to accommodate the larger sample.

**Three-electrode reference cell**
Reference measurements (polarization curves, standard galvanostatic tests and cyclic voltammetry) were conducted in a standard three-electrode setup using platinum wire and Ag/AgCl (3 M KCl) as the counter and reference electrode respectively. The cell itself was formed from an open-ended Teflon cylinder fitted with an O-ring at one end. The sample was then placed underneath and clamped in place using springs in order to obtain a defined surface area. This cell is shown schematically in Figure 9a and b.

**U-cell**
As discussed in Section 2.1, a reliable method for determining the current flowing through the bipolar electrode during an experiment is to divide the sample in two and measure the current externally with an ammeter. To recreate the conditions in the standard setup, a U-shaped canal was milled out of a solid Teflon piece with the dimensions 30 x 5 x 10 mm as shown in Figure 9c.
Arrays

Array experiments were performed in a larger cell made of plastic with a total size of 50 x 80 mm. Platinum foil was employed as the anodic feeder electrode. The cathodic electrode, however, consisted of a graphite sheet, due to its lower cost and to reduce the amount of hydrogen bubbles formed during the experiments. The electrolyte in these experiments was 0.1 M HCl.

3.3 Methods and Analysis

3.3.1 Electrochemical Characterisation

Contrary to bipolar electrochemistry, standard electrochemical techniques require a direct electric contact with the investigated sample (working electrode). The clear benefit of this is that either the current or the potential can be fully controlled continuously while the output is measured.

Chronopotentiometric (galvanostatic) techniques imply that the current through the system is controlled, while the potential is measured as a function of time\(^96\). An appropriately chosen constant current, assures a constant
rate for the electrochemical reactions. Chronopotentiometry is a very common approach to perform electrodeposition because it is straightforward to control the process parameters, such as the deposition rate and coating thickness, by adapting the current. Constant current mode was used to generate the outer field to form the corrosion gradients described in paper III-V, and to perform the deposition experiments in paper I.

In chronoamperometry, on the other hand, the potential is controlled while the resulting current response is measured\(^{96}\). In paper II constant potentials were applied between the feeder electrodes to induce the bipolar effect.

A versatile and common electrochemical technique that utilises a controlled potential is cyclic voltammetry (CV). During a CV the potential is scanned at a constant rate, back and forth, between two potentials a set number of times and the current response is measured\(^{96}\). The technique can provide information about electrochemical and chemical processes occurring in the system, within the set potential window.

Polarisation curves are a variation of a scanning potential method that is often applied to evaluate corrosion behaviour. Typically the sweep is started at a cathodic potential where the steel is stable, and scanned up to where dissolution of the metal proceeds. The logarithm of the total current, which represents the sum of the anodic and the cathodic currents, is then plotted against the potential\(^{76}\). A typical example of a curve for a standard stainless steel is shown in Figure 10. Initially, the total current is negative and the dominating reaction is the reduction of protons to hydrogen gas. As the potential is increased the metal starts to oxidise and a critical point is reached where the anodic current is equal to the cathodic, seen as a minimum in the plot, \(I_{\text{corr}}\). This potential is known as the mixed potential or corrosion potential, \(E_{\text{corr}}\). Beyond this point the oxidation of the surface continues and the anodic current increases. If the oxide film that forms is stable enough to protect the metal a maximum current is reached, \(I_{\text{passivation}}\), at the passivation potential, \(E_{\text{passivation}}\). After this the surface becomes passivated and the current drops and remains constant, \(I_{\text{passive}}\), because it is limited by the dissolution of the passive film. The increase in current from \(I_{\text{passive}}\) is caused by pits forming in this region. When the potential is increased further beyond the stability of the passive layer at \(E_{\text{transpassive}}\) the current increases even further while the surface corrodes, this is called the transpassive region.
3.3.2 Scanning droplet cell

The scanning droplet cell (SDC) technique is a relatively new concept for local electrochemical analysis\textsuperscript{97,98}. The basic setup consists of a capillary or cone, containing the counter and reference electrode and the electrolyte, with a small tip, mounted on a movable stage. The tip is moved close to the sample surface so that only a drop of the electrolyte is in contact, thus defining the working electrode. The area analysed, and thereby the resolution, will depend on the size of the tip and the wettability of the surface. A benefit of this approach, therefore, is that a sample will only be affected at the location of the tip. Since, on the whole, it is a standard three-electrode cell most common electrochemical techniques can be applied, such as cyclic voltammetry, chronopotentiometry or even impedance spectroscopy. There are a number of different types of SDC constructions adapted for various applications\textsuperscript{93,99–101}.

For the SDC analysis performed in paper IV, a polytetrafluoroethylene tip with a 1 mm diameter opening was used. The cell was mounted on motor-driven micrometer screws and a force sensor for positioning, and set up with a syringe pump system to control the electrolyte flow and exchange. The measurement itself was set up to perform a linear potential sweep with a scan rate of 2 mV/s, between -0.6 V and 1.5 V. A Pt-wire acted as counter...
electrode together with a Ag/AgCl (3 M KCl) reference electrode. 0.5 M Na₂SO₄ was chosen as the electrolyte.

3.3.3 Other characterisation techniques

Optical/visual, camera
A straightforward method of comparing the steel samples tested in this work was by the naked eye. A camera equipped with a flash and a circular polarizer, to reduce the effect of light reflected by the steel, was also used to document the steel samples. The polarizer gives the steel a slightly darker appearance than in reality.

Scanning electron microscopy (SEM)
SEM is a versatile technique that is, and has long been, a very common analysis method in both industry and academia. It can produce high resolution images at magnifications far beyond the capability of optical microscopes. The instrument generates a picture by a focused electron beam that is scanned over the surface of the sample. Each scanning point represents a pixel in the created image. The beam electrons can interact with the surface in different ways, and backscattered electrons (BSEs), or secondary electrons (SEs) are typically analysed. BSEs are electrons that scatter elastically when they interact with the surface and therefore keep most of their energy. A backscattered image gives more chemical information and the contrast in the image depends, amongst other things, on the atomic number of the elements in the sample. SEs, on the other hand, scatter inelastically and lose energy. They are commonly used to generate a more comprehensible image of the surface due to the fact that they give a higher aspect ratio and enhance surface topography.

The micrographs in this thesis were generated by detection of secondary electrons. Further details are presented in the respective papers. SEM was used to map the gradients by collecting a number of micrographs across the sample and compiling them using the photo merge feature in Adobe Photoshop. For the first samples the pits size and position on the pitting corrosion gradients were measured and counted manually from the micrographs. Continuing the work, however, a more effective way was necessary and the image processing and analysis programme ImageJ was used. The compiled micrographs of the gradients were first cut to only show a representative part of the gradient, then converted into black and white monochrome images. A threshold value was chosen to determine what the programme identify as a pit, then the analyse particles feature was employed to count and measure the pits. The same programme and process was also applied to analyse the gold nano-particle gradients in paper II.
X-ray photoelectron spectroscopy (XPS)

One of the most commonly used surface analysis techniques of today is XPS. It is based on the photoelectric effect and was developed in the 1960s by the group of Kai Siegbahn\textsuperscript{102}. The technique is extremely surface sensitive, typically probing only a few nanometres into the surface, and can provide quantitative information as well as insights into the chemical states of the analysed material. A sample irradiated with X-rays of a known energy can emit electrons due to the photoelectric effect, according to Einstein’s photoelectric law\textsuperscript{103}.

\[ E_k = h\nu - E_b - \varphi \]  \hspace{1cm} (2)

Where \( h\nu \) is the energy of the X-rays and \( \varphi \) is the work function of the spectrometer. The kinetic energy, \( E_k \), of the emitted photoelectron, thus, corresponds to the binding energy, \( E_b \), of the atomic orbital it comes from, which is specific to the element and the orbital. XPS spectra are thus given for specific orbitals, e.g., C1s, Cr2p, etc. The binding energy also depends on the chemical environment of the atom from which the electron is ejected, and so is useful for identification of different chemical species.

For the standard XPS measurements performed in paper I, a Phi Quantum 2000 XPS instrument, equipped with a hemispherical analyser. An Al K\( \alpha \) X-ray source with energy of 1468.7 eV was used.

HAXPES/HIKE

XPS is, as mentioned, an extremely surface sensitive technique. The probing depth achievable with the in-house equipment is only of the order of 2 nm; this is generally not deep enough to obtain a complete picture of passive films on materials, which are often thicker than the probing depth. As the probing depth is dependent on the kinetic energy of the photoelectron, it can be increased by increasing the energy of the incoming X-rays (eqn 2). Photoelectron spectroscopy using higher excitation energies is known as hard X-ray photoelectron spectroscopy (HAXPES) or high kinetic energy (HIKE). To achieve this, a synchrotron X-ray source is often used. In paper IV, the HAXPES measurements were performed utilising the HIKE end station at the KMC-1 beam line at the Helmholtz Zentrum BESSY II in Berlin. Two beam energies were chosen for the analysis, 2005 eV and 6015 eV, which corresponds to probing depths in steel of around 3 and 7 nm, respectively\textsuperscript{82}.

De-convolution of the spectra was performed using XPS-peak and Igor software, reference peak positions for the different materials were taken from the handbook of XPS\textsuperscript{104}, and the work of Biesinger et al.\textsuperscript{105}
4. Results and Discussion

“Science isn’t about why, it’s about why not!” Cave Johnson (Portal 2)

There are many fascinating and promising features to explore using bipolar electrochemistry. In this work the technique was used to induce gradients in different materials to evaluate new possible applications for electrodeposition and corrosion analysis. Both sides of the bipolar system, covering both cathodic and anodic processes, were studied to gain a deeper overall understanding of the possibilities of bipolar electrochemistry.

In this chapter, a summary of the results and discussions described in the appended papers is provided. These results are separated into two subsections according to the two poles of the bipolar electrode. The first section describes the experiments performed predominantly on the cathodic pole, specifically those related to electrodeposition applications. The second section will, subsequently, address the anodic pole and reactions taking place there, namely corrosion.
4.1 Cathode/ Bipolar Electrodeposition

As described in Section 2, reduction reactions on the cathodic edge of the bipolar electrode can be exploited for the electrodeposition of gradients in materials. In this work, two types of bipolar electrodeposition were evaluated. The first is a concept to explore how the cathodic pole can be employed to generate compositional gradients of different heavy metals to evaluate screening and recycling possibilities. The second approach demonstrates how the size of surface immobilised gold nanoparticles can be modified by bipolar electrochemistry.

4.1.1 Metal gradients

Electrodeposition is almost synonymous with the deposition of metal films from solutions of metal salts. One of the many applications of this process is in the recovery of different metals for recycling. This concept is well-established in, for example, wastewater treatment61. Bipolar electrochemical processes, such as those based on the fluidised bed reactors presented in the introduction, have long been considered for processes such as metal recovery19.

Put simply, metals deposit at different potentials, and bipolar electrodes have a gradient in potential. If the bipolar approach is applied to a solution containing a mixture of different metals, these will deposit at different locations along a bipolar surface according to their respective redox potential47,48,106. In this thesis, this concept was initially explored with respect to the possibility of screening a complex solution of metals and subsequently separating those metals from dissolved fly ash. This was first investigated with a series of bipolar experiments with electrolytes containing controlled mixtures of different metal salts.

The metals selected were copper, lead, cadmium and zinc due to the fact that they are very common and that they are relevant to recover for environmental reasons. Different electrolyte combinations of the three were prepared to obtain similar concentrations of the respective ions as in solutions of dissolved fly ash. The different combinations investigated were Cu, Cd (Sample 1), Cu, Pb (Sample 2), Cd, Pb (Sample 3) and Cu, Cd, Pb, Zn (Sample 4). Silicon wafers with a 2000 Å layer of sputtered gold, cut into 10 x 20 mm pieces, were used as substrates. These substrates were then placed in a setup with a chosen electrolyte and exposed to an external electric field by applying 0.2 A between the two feeder electrodes for 150 s. During the experiments the samples acted as bipolar electrodes. This was obvious by the formation of oxygen bubbles on the anodic edge of the sample, and that on the cathodic edge a clear gradient of reduced metals could be observed as a col-
our shift, as seen on sample 4 shown in Figure 11. It should be noted that part of the deposit was observed to be formed of loosely attached particles which were easily lost into the solution when the sample was removed from the electrolyte.

![Figure 11. Photograph of sample 4 (Cu, Cd, Pb, Zn).](image)

One sample prepared with each electrolyte combination was further evaluated. XPS analysis was performed along the cathodic edge of the four samples. Figure 12 depicts the relative intensities of the different metals along the different samples.

![Figure 12. Relative intensities of metals across samples 1-4 as determined from XPS analysis.](image)

Gradients in the co-deposited metals can be observed on all samples. The trends in the relative amounts of metal deposited follow the behaviour expected according to the reduction potentials, i.e.,

\[ Zn < Cd < Pb < Cu \]
This is seen most clearly for samples 1 and 4. For sample 1, it can be seen that very little Cd was deposited at distances more than 6 mm from the cathodic edge, while copper was deposited at all positions measured. The reduction potentials of Cu and Cd are about 0.75 V apart at standard conditions. A similar trend in the distribution of Cd and Cu is seen for sample 4. Additionally, the majority of the deposited Zn on this sample was found only within 2 mm from the edge. The comparably smaller amount of Cu closer to the cathodic edge of the samples is possibly because the other metals have deposited on top, limiting the Cu-signal.

Furthermore, a clear increase in the thickness of the overall deposit can be observed via the decreasing Au signal towards the cathodic edge on samples 3 and 4. This gradient is not evident for samples 1 and 2, and this may be for two reasons. Firstly, the higher reduction potential of Cu causes it to deposit over a greater part of the electrode, explaining why Au is still visible in sample 3, where no Cu is present. Secondly, the lower ionic strength of the electrolytes used for the first three (two-component) samples compared to the last (four-component) sample should result in a higher electrolyte resistance. This can be expected to result in a larger gradient in the solution potential across the bipolar electrode, thus creating a longer gradient in the electrode-deposited metals. That is, on sample 4, the total cathodic current may only pass over a smaller distance from the edge, explaining the shorter gradient in this case.

To test the feasibility of applying this approach for screening and extracting metals from fly ash, a sample was created by applying the above settings for an electrolyte prepared by dissolving fly ash into concentrated hydrochloric acid, diluting, and adjusting the pH to around 3, a value similar to that used in the screening experiments. The results following XPS analysis are summarised in Figure 13, while the content of the dissolved fly ash as determined by ICP analysis is presented in Table 2.
Figure 13. Relative intensities of metals across the sample prepared from the dissolved fly ash solution, as determined by XPS analysis.

Table 2. Metal concentrations in the electrolyte prepared from dissolved fly ash.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>30.3</td>
</tr>
<tr>
<td>Zn</td>
<td>762</td>
</tr>
<tr>
<td>Pb</td>
<td>90.8</td>
</tr>
<tr>
<td>Cd</td>
<td>3.65</td>
</tr>
</tbody>
</table>

The results show a gradient in the thickness of the deposit, as evident from the decreasing gold signal towards the cathodic edge, however, it is much shorter compared to the references. This is probably because of the higher ionic strength of the ash solution, which would be expected to cause a shorter gradient in the deposit, as discussed previously for sample 4.

The signals from the metals present in the fly ash were dominated by Cu. Negligible amounts of the other metals, with the exception of a small amount of Zn, were detected. This is in stark contrast to the reference samples and the true content of the ash, which contained a relatively large amount of Pb. No Cd was detected, despite being easily detected in the initial experiments. It could be speculated that, as with the reference samples, part of the deposited material was seen to detach from the sample when it was removed from the cell. This may mean that deposited Cd or Pb may have been lost to the solution and therefore not detected in the surface analysis.

The sensitivity to electrolyte composition suggests that this approach, used in this manner, is not suitable as a screening method. Despite these drawbacks, it has been demonstrated that compositional gradients could be readily produced by this approach. Optimisation of the conditions, particularly the electrolyte composition, may be necessary for further refinement.
4.1.2 Gold Nanoparticles

Surfaces with chemisorbed nanoparticles have many possible applications in, for example, biosensors or screening. A number of approaches have been investigated to generate different variations of these types of surfaces that are typically generated by the self-assembly of dithiols on gold substrates decorated with chemisorbed nanometre sized gold nanoparticles.

In paper II, two different types of substrates pre-modified with gold nanoparticles were evaluated. The aim of the experiments was to explore whether a particle size gradient could be introduced across the samples by bipolar electrodeposition. An additional aim was also to evaluate the possibility to link the volume of deposited gold to the predicted current density profile. The first of the tested substrates had an even particle distribution across the entire surface, and a particle density of 10%. The second substrate had a gradient in particle density ranging from around 1% to 20%. This sample was used to evaluate the viability of the method for generating two orthogonal gradients.

In order to establish the necessary external field strength in the bipolar experiments, the reduction potential of gold onto the nanoparticle substrates was determined in a standard three-electrode experiment. A potential of 0.73 V vs. Ag/AgCl (3 M KCl) was observed to be sufficient to reduce gold on the substrates. In the bipolar system, therefore, the corresponding potential difference between the surface and the electrolyte at the cathodic pole must, at some point, exceed this potential to initiate the deposition of Au. Preferably, to generate a gradient, this point should occur some distance from the edge. An external potential of 6 V was experimentally determined to provide a sufficient potential drop in the current setup, with a feeder electrode separation of 4 cm and a sample length of 1 cm. A schematic of the procedure is depicted in Figure 14. When nanoparticle covered substrates were exposed to an external potential of 6 V, the bipolar effect became visible by a colour shift to purple at the cathodic edge. This shift occurs because spherical gold nanoparticles can induce localised surface plasmon resonance, which in turn depends on their size. Therefore as their sizes increase, due to gold deposition onto them, a colour change is observed. Larger particles produce a more intense and darker colour. An increase in feeder potential to 7 V caused the colour shift to appear further from the cathodic edge of the sample, as predicted.
Figure 14. Schematic of a thiolated gold substrate decorated with gold nanoparticles, placed in a bipolar setup.

Single gradients

The substrate with uniform particle coverage was modified using bipolar electrodeposition by applying a constant outer potential of 6 V for 25 sec. During the experiment the reduction on the particles was again visible to the naked eye by a purple colour shift starting from the cathodic edge. At the anodic pole the main reaction taking place was electrolyte decomposition (water oxidation). A partial oxidation of the dithiol layer, and the dissolution of some nanoparticles, could also be observed at the anodic edge. However, since the electrolyte was in excess, it was concluded that these reactions did not limit the bipolar current. Thorough SEM mapping of the samples was performed to evaluate the size distribution of the nanoparticles across the surface. Figure 15 depicts five micrographs of the particle size gradient induced by the bipolar electrodeposition on the uniform sample.

Figure 15. SEM images from the cathodic pole after the bipolar deposition, on the surface with a 10% particle coverage. Distance from the cathodic edge is indicated above each frame.

At the cathodic edge the particles grew considerably, since the reducing potential was highest at this point. Towards the middle, where the driving force for reduction was smaller, the particles were correspondingly smaller, and 5 mm in from the cathodic edge none of the particles had grown.
No gold deposition could be observed on the underlying substrate. This indicates that the dithiol layer was of sufficient thickness and coverage to protect the underlying surface. Thus, the majority of the cathodic current was assumed to pass via the deposition of gold onto the particles. Further, this means that the reaction of the particles will determine the bipolar current. Therefore, the size of the particles across the gradient can provide an indication of how the current density along the cathodic pole was distributed. To generate an approximation of the current profile along the sample, the volume of deposited gold was estimated by calculating the area of the particles within the micrographs in Figure 15. Only particles with a diameter larger than 11 nm were counted and the particles were then assumed to be hemispheres. The results are depicted in Figure 16a.

![Figure 16](image.png)

**Figure 16.** a) Volume of deposited gold, calculated from the micrographs in Figure 15, as a function of distance from the cathodic edge. b) Fraction of particles >11 nm, as a function of distance from the cathodic edge.

The amount of gold appears to increase exponentially towards the cathodic edge from the middle of the sample. The shape of the curve in Figure 16a is similar to that of the modelled current distribution across a macro scale bipolar electrode. Analysing the volume of deposited gold along the surface...
could, thus, indirectly give an estimate of the current profile, which is otherwise difficult to assess along a bipolar electrode.

It should be noted that the electron tunnelling between the particles and underlying substrate has an influence of the amount of deposited gold and which particles grow. The current takes the path of least resistance, therefore, if some particles provide a path of less resistance by having more favourable tunnelling condition or shape, these grow faster than others. This can be observed as an uneven particle size distribution (Figure 15). Hence, for an additional comparison, to evaluate the particle growth, the fraction of particles which showed evidence of gold deposition was plotted vs. distance from the cathodic edge. Almost all of the particles had a diameter greater than 11 nm at a distance 1 mm from the cathodic edge. Unsurprisingly, at the centre of the sample only about 10% of the particles had grown, as shown in Figure 16b. The general trend of the curve seems to follow the expected S-shape.

**Double gradients**

As described in Section 2.2.1, the number of particles per surface area on the dithiol-modified substrates can be fine-tuned by changing the deposition methodology. By combining this feature with the bipolar electrodeposition performed on the first sample, there is an opportunity to form two-dimensional gradients. That is, surfaces with orthogonal gradients in both particle density and size can be generated. A substrate with the particle density gradient placed perpendicular to the field was modified in the bipolar setup by a 25 sec exposure to 6 V. Figure 17 displays twelve micrographs of the resulting double gradient.
Figure 17. SEM images of the different parts of the two-dimensional gradient. Distance from the cathodic edge is indicated along the top, with the particle density indicated on the right-hand edge.

The top and bottom rows in the figure are the parts of the substrate with high and low particle densities, respectively. A gradient in particle size, from large at the cathodic edge to small near the middle, can be observed for all particle densities. Thus, a substrate with two orthogonal gradients, one in size and one in particle density, could be formed using bipolar electrochemistry.

Where the particle density was initially low, i.e., 1%, particles at the cathodic edge grew considerably more than those in the 10 and 20% regions. This is most likely because where there are fewer particles, there are a smaller number of reaction sites: thus, a larger fraction of the current passes through each particle, causing them to grow more rapidly. Alternatively, a lower particle density also means that there is a lower chance of depletion of gold ions at the nanoparticle surface due to overlapping diffusion layers with neighbouring particles, and this may also influence the growth rate of the particles.

The volume of gold deposited across these regions of interest was estimated in the same way as for the single particle density gradients. The results are presented in Figure 18.
It is observed that more gold has been deposited in all of the density regions (up to ~1.5 × 10^6 nm^3) compared to the single gradient (up to ~0.8 × 10^6 nm^3). This may be because of a thinner dithiol layer on the substrate, due to a necessary drying step of the substrate prior to the preparation of the particle gradient; in which case the particles will be closer to the underlying surface, which makes them more reactive. Another observation is that the deposited volume up to about 2 mm from the edge looks more or less constant for all particle densities. A possible reason for this is that the growth here becomes diffusion limited.

In addition, it is noted that the total volume of gold is similar for all particle densities, despite the very different particle densities themselves. This observation supports the previous assumption that individual particles in low density regions are subject to higher current densities and grow faster as a result.

The bipolar approach proved to be a successful strategy to generate samples with orthogonal gradients. Surfaces with these structures have many advantageous properties in fields where combinatorial studies are required.
4.2 Anode/Corrosion screening

As described in Sections 2.2.2 and 3.3.1, common ways to study corrosion properties often involve exposing the material to oxidising potentials of different magnitudes, or the use of potentiodynamic electrochemical measurements, such as polarisation curves. Many of these methods are comparatively slow and ultimately destructive, making it difficult to visually study different degrees of damage. However, along the anodic pole of a bipolar electrode there will be a gradient in oxidation reactions, which will subsequently create a gradient in corrosion damage, depending on the materials and conditions. This, in turn, can provide a way to evaluate the corrosion properties of the material under study. Thus, when used in this way bipolar electrochemistry can provide a good complement to the standard methods by providing an illustrative way to show the proceeding corrosion damage.

The results in the following section demonstrate how bipolar electrochemistry can be exploited to induce corrosion gradients for the purpose of evaluating corrosion properties. The first part introduces the initial development of the method. In the second part, an in-depth study of the factors influencing the formation of a corrosion gradient on a steel sample is performed. Finally, two methods for high throughput testing are described.

4.2.1 Corrosion gradients

Initially, grade 304 stainless steel was studied in setups with two different types of electrolytes, as described in the experimental section. Sulphuric acid was initially investigated, due to its industrial relevance, with the equally commonly occurring hydrochloric acid, used in following experiments. The 304 grade was chosen because it is the most common steel in use today. The purpose of this study was to introduce the concept of utilizing bipolar electrochemistry for corrosion screening. This work is presented in paper III.

In a sulphuric acid electrolyte the corrosion damage on the samples progressed slowly, but the development of an obvious gradient, approximately 4.5 mm from the anodic edge and approximately 1.5 mm in length, could be observed over a period of two hours. Corrosion could not be observed with the naked eye closer to the middle of the sample. Compiled scanning electron micrographs, shown in Figure 19, display how the damage proceeded along the sample, from the severely corroded region on the left at the anodic edge to the visually unaffected region closer to the cathodic edge, seen on the right.
The first signs of corrosion appear at the grain boundaries, consistent with the behaviour expected for this system. When moving towards the anodic edge the attack becomes increasingly severe because of the larger anodic potential. At the extreme edge of the anodic pole, the current density is highest and the whole region is continuously etched. No specific differences could be observed between the anodic edge and the visible start the gradient, 4.5 mm from the edge. Even though the gradient is short, compared to the whole sample length, it still provides an interesting view of how the corrosion damage proceeds on SS304 in sulphuric acid. However, a more effective approach, such as a shorter experimental time or a longer gradient for better resolution, would be beneficial.

The electrolyte composition is of utmost importance to the corrosion behaviour of the material tested. Since the corrosion gradients generated in the sulphuric acid were difficult to assess quantitatively, hydrochloric acid was tested as an electrolyte. Unlike sulphate, chloride ions are known to attack the passive layer on stainless steel and cause pitting corrosion, as described in Section 2.2.2. In HCl, gradients on the 304 steel formed within minutes rather than hours, at lower potentials, and extended across a greater distance from the anodic edge, making visual analysis more straightforward. Thus, HCl was found to be more effective for fast corrosion screening of stainless steels in this type of setup. The most suitable settings were found to be in a 0.1 M HCl electrolyte with an applied current of 0.2 A for 15 minutes. In order to evaluate the corrosion damage further, SEM was used to map the gradients in high resolution. The top half of Figure 20 depicts a pitting corrosion gradient formed using the above mentioned settings.
Figure 20. Above) gradient in pitting corrosion on SS 304 (anodic edge on the left. Image compiled from 8 individual micrographs). Below) micrographs from the reference samples, 25, 10 and 5 mA cm$^{-2}$, respectively.

Pit formation was observed from approximately 7 mm from the anodic edge with a continuous increase in pit size towards the edge. Along the sample different stages of pitting corrosion damage can, hence, be found. Based on a visual comparison the change in pit size across the anodic pole seems to follow the predicted potential drop across a macro scale bipolar electrode$^{22}$, qualitatively supporting the existing theory. To further visualize the pit size distribution across the gradient, the pit sizes were measured and plotted as a function of their distance from the anodic edge, as seen in Figure 21.

Figure 21. Pit size as a function of distance from the anodic edge, the marked positions represent the size of pits formed in the reference measurements.
This plot emphasises how a few large pits form close to the anodic edge and many small pits form closer to the centre of the sample. The solid lines indicate the mean and one standard deviation. The general shape of the size distribution curve can be compared with, and is well matched to, the predicted current density\textsuperscript{16}, where the current decreases exponentially from the edge to the centre. Nevertheless, the exact potential and current density at each point remains unknown. Thus, reference measurements in a three-electrode setup were made with constant currents in order to compare these pits with pit sizes across the gradient (Figure 20, lower). The marked positions in Figure 21, represent the size of the pits formed in the three-electrode setup by applying three different current densities, 5, 10 and 25 mA cm\textsuperscript{-2} respectively. Overall, the reference measurements are seen to correspond well with the expected exponential current decline across the anodic pole.

To employ bipolar electrochemistry for the generation of corrosion gradients in stainless steel presented promising results. However, a deeper understanding of the factors influencing the gradient formation is necessary if the approach is to be utilised further or expanded to different materials and electrolytes. Particular factors of interest include the magnitude of the feeder current and the initiation of pitting corrosion on the gradient itself.

4.2.2 In-depth analysis of the gradients

To gain a deeper understanding of how pitting corrosion gradients form, a series of experiments were set up with varying exposure time and bipolar field strength. 304 steel samples with a size of 20 x 10 mm were immersed in 0.1 M HCl and exposed to different external potentials, by changing the feeder current. The selected feeder currents were 50, 75 and 100 mA, applied for either 6 seconds or 10 minutes. The distance between the feeder electrodes was kept constant at 30 mm. This work is further presented in paper IV.

A short exposure time (6 s) was chosen as the time at which the very first initiation of damage became visible by eye. During the course of the experiments the effect of the change in the feeder current was made obvious by visual observation alone, as is depicted by the photos of the different samples (Figure 22a).
An increase in the field strength, by applying a larger feeder current, causes the visual initiation of pits to move further away from the anodic edge, from around 2 mm in for the 50 mA sample to 4 mm for the 100 mA sample. The reason for this change in the pit initiation region is the response of the steel surface to the applied potential gradient.

It is known that an increased anodic potential increases the probability of pit initiation. It has also been demonstrated that an increased potential causes an increase in thickness of the passive film on steel in a HCl electrolyte, and that this can slow down the rate of pit growth. The pit distribution across the three samples seems to match with these expectations. That is, the smallest feeder current induces the smallest potential difference across the sample and the growth of the passive film will, therefore, be slower. Even so, the potential is sufficient to induce pitting corrosion in the thinner film. An increase in feeder current generates a thicker passive film at the anodic edge, which is more resistant to pitting. Fewer pits, therefore, initiate at the anodic edge under these conditions.

The local potential and current density is expected to be similar for each sample in the region where pit initiation is seen to occur, which will be located further from the anodic edge with increasing feeder current.
The longer exposure time (10 min) caused, as predicted, severe damage to the anodic edge (Figure 22b). For the higher feeder currents of 75 and 100 mA, the distribution of pits was observed to change significantly over time. New pits were seen to form closer to the anodic edge, which subsequently grew faster than those which appeared within the first few seconds. The observations seem to be consistent with those made for the short time experiments, in that there is a competition between further passivation and pit initiation at the anodic edge. That is, as the samples are exposed for a longer time, the passive film can only grow to certain extent while pits still can and will form at high anodic potentials.

SEM analysis was performed to further investigate the corrosion damage along the gradients formed during the 10 min experiments. The results, seen in Figure 23, further show how a change in feeder current influences the pit size and morphology.

![Figure 23](image)

Figure 23. SEM images depicting pit morphology across the anodic edges of the 10 minute samples. (The scales of the individual micrographs have been adjusted so as to clearly visualise the pits).

Pits at the anodic edge of the 50 mA sample (upper left corner in Figure 23), and further from the edge on the higher feeder current samples, show evidence of having pit covers; the mesh-like structure seen in some of the micrographs. Pit covers have been suggested to form to a greater extent on steels with a thicker oxide. The open pits seen in the lower left corner, on the other hand, occur more frequently on weaker passive films under stress. At the anodic edge of the 50 mA gradient, pits are covered, indicating a thicker passive film. Unsurprisingly, for the higher feeder currents the surface closest to the anodic edge is under more stress, and open pits form. The large uncovered pits observed on the edge of the 100 mA gradient also indicate
that a higher current passes through this region. Thus, a clear trend in the location and type of pit formed was observed to follow the expected potential and current density profile across the samples.

The visual analysis of the corrosion gradients generated by different feeder currents and exposure times established that, on a short time scale, the passive oxide layer prevents pit formation at the anodic edge, where one might otherwise expect higher current densities. Over time, however, the film breaks down and pits form as expected. This oxide passivation was also observed to play a key role in controlling the pit morphology when the current was varied. Furthermore, the feeder current is observed to have a strong influence on gradients formed. This demonstrates that the part of the current passing through the steel sample during the experiments changes when the feeder current is changed.

**Bipolar current**

The total current through the system will always be the sum of the bipolar current and the current through only the electrolyte. As discussed previously, the magnitude of the current through the alternative routes will depend on a number of factors such as, the scale of the system, the conductivity of the electrolyte and the possible reactions. A cell was set up using a split electrode setup for the purpose of measuring the actual bipolar current through the steel sample during an experiment. The electrolyte was 0.1 M HCl, and the feeder electrode distance was 3 cm. The three different feeder currents evaluated previously were applied in the cell. The results are seen in Figure 24.

![Figure 24. Bipolar current (ibpe) through a steel bipolar electrode upon application of feeder currents of 50, 75 and 100 mA in 0.1 M HCl. Other cell parameters (dimensions, etc) are as for the corrosion screening setup in the previous section.](image-url)
Interestingly, the part of the total current that took the bipolar path increased from around 50% to 70% when the feeder current was changed from 50 to 100 mA. This can be explained by considering the bipolar electrode as having a non-Ohmic overall resistance, due to charge transfer reactions, in parallel with the Ohmic electrolyte resistance. Consequently, the bipolar current varies non-linearly with the applied feeder current and the fraction of the total current passing through the bipolar electrode changes as a result. The slight current increase over time is likely a result of the increase in active surface area as the samples corrode.

**Scanning Droplet Cell (SDC)**

The visual analysis and the bipolar current measurements of the different gradients indicate that the passive film along the gradients changes which has a strong influence on the pitting corrosion. Because of its ability to perform spatially-resolved electrochemical analysis of a surface, a scanning droplet cell was used to evaluate corrosion properties along the gradients. The automated SDC setup was programmed to measure an array of positions across the different samples and to apply a linear potential sweep at each position.

A SDC only measures the surface directly under the probe, and the quality of an untreated passive film on steel can vary. Therefore, reference measurements were conducted to establish that the variations seen for the samples were actually introduced by the bipolar experiment. Three different references were evaluated; one that only had been polished and placed in ambient conditions and two that had been pre-exposed to HCl for 6 s and 10 min, respectively. Polarisation curves from the reference analysis are seen in Figure 25.
When the polished steel was tested, the shapes of the polarisation curves from different positions were very different (Figure 25a). On the other hand, when the samples that had been immersed in 0.1 M HCl were analysed in the same way, the curves were found to be very similar, as seen in Figure 25b and c. Thus, the exposure to acid makes the surface of the samples more homogeneous. A longer exposure to HCl is also observed to shift the $E_{\text{corr}}$ of the steel to slightly more negative potentials indicating that the acid etches the passive film on the steel (Figure 25c). The uniformity of the reference measurements performed on the acid treated steel confirmed that eventual variations seen in the analysis of gradient samples can be attributed to their previous treatment in the bipolar setup.

When SDC array scans were applied to samples with pre-prepared corrosion gradients, clear changes in the shape of the polarisation curves at different positions across the gradients could be observed. The positions were chosen according to the schematic seen in Figure 26. Figure 27a to c depicts polarisation curves from the short exposure (6 s) samples.
Figure 26. Schematic of the programmed measuring positions for the SDC analysis.

Figure 27. Polarisation curves at each position for the a) 6 s, 50 mA sample, b) 6 s, 75 mA sample, c) 6 s, 100 mA sample.

For each of the measured gradients, the corrosion potential, $E_{\text{corr}}$, shifts towards lower potentials from the anodic edge (black curve) towards the middle (green curve) of the samples. This confirms, as expected, that at the anodic edge the surface is oxidised to a greater extent than it is closer to the middle. The curves also become more similar in both shape and $E_{\text{corr}}$ values closer to the centre of the sample, which corresponds well to the predicted potential drop across a bipolar electrode\textsuperscript{10}. None of the curves exhibit $E_{\text{corr}}$ values that coincide with those of the reference sample, indicating that even
at the middle of the sample the surface is influenced by the bipolar gradient. While this trend is seen across all gradients to different extents, it is more pronounced on the samples exposed to a larger feeder current. Similar trends are seen when analysing the samples exposed for 10 min in the SDC setup, as shown in Figure 28. With the longer exposure time, $E_{\text{corr}}$ shifts to even higher potentials at the anodic edge for all of the samples.

Figure 28. Polarisation curves at each position for the a) 10 minute, 50 mA sample, b) the 10 minute, 75 mA sample, c) 10 minute, 100 mA sample. The innermost row (green in Fig 27) was removed due to contamination of the probe.

Interestingly, the difference in $E_{\text{corr}}$ across the length of the gradient is smaller for the 10 minute experiments. The curves corresponding to measurements at the edge are more similar when compared with curves measured on the samples exposed for 6 s. When the steels are exposed for a longer time, the surface at extreme the anodic edge becomes passivated to the extent that the reactions are significantly limited. This will change the current distribution across the sample, levelling it out at the anodic edge and moving the reaction front further in towards the middle of the sample.

The results from the SDC analysis indicate that a 6 s exposure to a feeder current effects a continuous shift in $E_{\text{corr}}$ from the unaffected centre of the
sample to the anodic edge, even though pit initiation was generally not observed at the anodic edge on this timescale. This is consistent with the conclusions of the previous visual analyses (Figure 22 & Figure 23).

**HAXPES**

To more thoroughly study the formation of the passive film and its properties on a steel behaving as bipolar electrode, HAXPES measurements were performed. The higher x-ray energy allows for, on the length scales of the passive film, a deep probing of the sample surface, which means a more complete picture of the composition of the passive layer can be obtained. A sample that had been exposed to a 100 mA feeder current for 6 s in 0.1 M HCl, together with a reference immersed in the same acid for 6 s, were chosen for the study. The two beam energies used, 2 keV and 6 keV, provide compositional information of the surfaces at depths of up to 3 and 7 nm, respectively. Three positions along the gradient were analysed, one 1 mm in from the anodic edge, the second in the middle of the gradient, and the last close to the middle of the sample.

Summaries of the relative intensities of iron and chromium at the different positions, and compared with the reference, are presented in Figure 29. When comparing the relative intensities of iron, chromium and nickel from the 2 keV measurements, a higher chromium content was observed at the anodic edge compared with the centre of the gradient and for the 6 s reference sample. The low iron content at the anodic edge of the sample, compared with the reference, is because chromium is enriched at the surface due to selective dissolution of iron oxides in an acidic environment and anodising potentials. The nickel content seemed uninfluenced by the bipolar experiment.
De-convolutions of individual metal spectra for iron and chromium were also carried out in more detail to obtain an estimation of the oxidation states. The relative intensities of the different oxidation states are presented in Figure 30.

On the whole gradient sample, close to 50% of the Fe within 3 nm of the surface is in the metallic state. The proportion decreases only slightly closer
to the anodic edge. On the reference sample, however, 45% of the iron was in the metallic state. For the higher beam energy, i.e., deeper down below the surface, more of the iron was in elemental form. All positions on the gradient sample were found similar. Again, the reference had a lower amount of metallic iron, which is likely because of a lower dissolution rate of the oxidised iron on the reference sample. Only 11% of the chromium was in metallic state in the top 3 nm of the surface layer at the anodic edge. This proportion increases towards the centre of the sample, with the reference showing the strongest Cr$^0$-peak. A larger proportion of metallic Cr was found at deeper probing depths, with a similar proportion of Cr$^0$ at the 1 mm and 3 mm positions. At the 9 mm position, a higher proportion of Cr$^0$ than in the reference sample was found.

Closer inspection of the HAXPES spectra shows that the relative amount of chromium hydroxide compared to the oxide decreased when moving from the anodic edge to the middle of the sample. The reference sample contained the smallest amount of hydroxide. This can be seen in the de-convolutions of Cr2p spectra, as shown in Figure 31.

![Figure 31. (Upper) De-convolutions of the Cr2p peaks for P1 (1 mm), P2 (3 mm) and P3 (9 mm) and the reference from the 2 keV analysis. (Lower) De-convolutions of the Cr2p peaks for P1 (1 mm), P2 (3 mm) and P3 (9 mm) and the reference from the 6 keV analysis.](image)

Together these results indicate that a thicker and more oxidised passive layer formed at the anodic edge. These observations confirm the previous visual
and SDC analysis, which indicated further passivation of the steel towards the anodic edge.

In summary, the in-depth study of the corrosion gradient shows that the setup is very sensitive to changes in the feeder current, and that the applied feeder current strongly influences the formed gradient. It is also evident that only 6 s is sufficient to generate a gradient across the samples even at low feeder currents. This sensitivity thus requires careful consideration of the experimental parameters when designing experiments for specific studies. This sensitivity, however, could be beneficial depending on the aim of the intended study. For example, as demonstrated here, the early stages of corrosion can be studied with low currents and short times, while if the effect of more extensive corrosion is of interest, a higher feeder current and longer time can be applied.

4.2.3 Corrosion screening arrays

Previous studies have established that multiple objects can act as individual bipolar electrodes when an external electric field is applied. In paper V, this strategy was combined with the corrosion gradient approach in paper III as a method to perform simultaneous, high-throughput screening of different steels.

Reference arrays

To establish that identical steel samples behave identically when exposed together in the same bipolar cell, experiments with only one type of steel were first performed. Three samples of 304 steel were placed together in a cell equidistant from each other and the feeder electrodes, and simultaneously subjected to an external electric field. The same experiment was also performed for three samples of 2205 steel for comparison purposes. 2205 steel is a grade noted for its high resistance to pitting corrosion.

As seen in the left-hand photographs in Figure 32, all three 304 samples displayed very similar gradients with respect to corrosion damage, while the 2205 samples appears undamaged. This demonstrates that each sample will act as an individual bipolar electrode during the experiment.
This approach was subsequently employed to study if different steels can be studied in the same array. The sample matrix was, therefore, extended with three additional steel grades, MV, SK and SL, with different corrosion properties. The corrosion gradient-forming behaviour of each grade was initially investigated by testing three samples in the same array as shown previously for 304 and 2205; these experiments were taken to be reference measurements. It was consistently demonstrated that when samples of the same type are placed together in an array and subjected to the same conditions, each sample exhibits the same degree of corrosion.

The corrosion resistance of each steel grade was also investigated in three-electrode experiments by performing linear potential sweeps and plotting their respective polarisation curves, as shown in Figure 33, as a standard test in order to verify their properties and enable a comparison.
Figure 33. Polarisation curves from standard three-electrode measurements for the five different steels evaluated for the array experiments. Electrolyte: 0.1 M HCl, scan rate: 2 mV s⁻¹, surface area: 0.2 cm², ref. electrode: Ag/AgCl/3 M KCl

All samples showed corrosion behaviour in accordance with their PRE-numbers (i.e., 2205 > SL > SK > 304 > MV, see Table 1 on page 25) in these experiments, and the results were also in agreement with the degree of damage observed in the bipolar setup. The polarisation curves for 304 and 2205 are seen in the upper part of Figure 33. The most distinct feature is the much larger passive region for the 2205 sample. Similar properties are seen for SL in the lower part of the figure. SK is a steel with intermediate resistance, while MV is the least resistant steel of the five steels.

Mixed arrays
With established references, different kinds of steels can be compared in the same array to study how, or if, they influence each other. First, the 304 steel was compared in arrays alongside the 2205 grade. Here, the bipolar behaviour was, again, confirmed with the observation of hydrogen evolution at the cathodic end of all samples. However, the samples displayed very different behaviour at the anodic part as seen in Figure 34a. The pitting corrosion gradients on the 304 steel differed slightly from those observed in the reference arrays, in that they showed signs of more extensive damage. The damage was similar to that observed for the samples exposed to higher feeder currents in the previous section. The 2205 samples, on the other hand, displayed no evidence of pitting damage at all. The increase in damage and
altered shape of the gradient on the 304 steel indicate that the distribution of the bipolar current between the different individual bipolar electrodes was uneven during the experiment, with a greater proportion passing through the less corrosion-resistant sample.

Figure 34. Photographs of the steel samples after the different array experiments. a,b,c,d) denote the combination of samples in each array.

To further analyse this effect, the three other steel grades (SK, MV and SL) were placed in an array together and exposed to the same field (Figure 34b). As before, the most resistant steel showed no evidence of pitting damage, while the less resistant steels displayed more severe damage, relative to their respective reference measurements, with a clear pitting corrosion gradient. These results, therefore, confirm the presence of an uneven current distribution between the different steel grades.

Similarly, when the three least resistant steel grades (SK, MV and 304) were analysed together (Figure 34c), the most resistant of the three corroded less severely when compared with the same samples from the reference array. The opposite was true for the least resistant. That is, steels with a lower corrosion resistance corrode more severely compared to their respective references, when analysed in an array alongside more resistant steels (cf. 304 and 2205). It is therefore clear that in an array of steels of unequal corrosion resistance, the bipolar current will be divided unequally according to the corrosion resistances of the individual electrodes. Neither of the two most
resistant steel grades *Figure 34d*, showed any pitting corrosion damage when compared in the same array. This indicates that more aggressive experimental conditions would be required to study these samples thoroughly.

In summary, the concept of expanding the bipolar corrosion screening approach to arrays of samples has been successfully demonstrated. This approach is a simple and fast method for obtaining a general overview of the corrosion properties of different materials. In principle, these arrays could be expanded to a considerably larger number of samples than investigated in this preliminary work.

The unequal current distribution between different steels may be problematic for quantitative analysis. It would not be straightforward, for example, to obtain characteristic information about the gradients formed on specific steels in specific electrolytes (e.g., *Figure 21* on page 45), if the degree of corrosion damage varies depending on other nearby samples with different properties. However, this effect may yet prove useful qualitatively as it could enhance differences between otherwise similar grades of steel to make visual comparison easier.

### 4.2.4 Corrosion evaluation of TiAl

The idea for the corrosion evaluation of TiAl alloys was based on the same principle as the array experiments. However, instead of having multiple samples with different corrosion properties, a single sample with a compositional gradient was studied. The interesting aspect of this is the opportunity to perform two-dimensional screening. If the compositional gradient is placed perpendicular to the bipolar field all possible combinations can be analysed simultaneously.

Thin films of a titanium-aluminium alloy with a continuous compositional gradient of Ti and Al, were tested as a proof of concept. The underlying substrate was a circular silicon wafer with a diameter of 10 cm. The compositional gradient across the substrate ranged between 36% Ti and 64% Al, to 61% Ti and 39% Al. These samples were then placed in 0.3 M oxalic acid and exposed to a 0.8 A feeder current for 20 min. SEM analysis was performed on the sample before and after the bipolar experiment. *Figure 35* depicts micrographs from the different regions of the surface. The initial surface structure is different for the Al and Ti rich regions (*Figure 35a* and *b*). After the bipolar experiment corrosion damage could predominantly be observed across the Al-rich regions of the sample (*Figure 35c* and *e*)
The Al-rich region of the sample that was on the anodic edge appeared to have corroded severely (Figure 35e) compared to the reference. The Ti-rich parts of the film, on the other hand, were more corrosion resistant and showed almost no evidence of damage (Figure 35f). The same effect of uneven current distribution that influenced the screening arrays described in the previous section has a similar effect here, that is, causing the part of the surface that is more susceptible to corrosion to corrode even further.

Interestingly, some parts of the samples displayed corrosion damage on the cathodic as well as the anodic edge (Figure 35c). This is because of the amphoteric nature of the aluminium oxide and the increase in pH generated at the cathodic edge of the sample. The aluminium-rich parts of the film hence displayed a surface where the aluminium oxide had dissolved and left a porous structure of titanium oxide. At the titanium rich side of the sample, on the other hand, the cathodic edge did not show any signs of damage.

In summary, the principle of corrosion screening a compositional gradient has been successfully demonstrated. The ability to create such samples with two orthogonal gradients is an interesting concept for future development of high-throughput screening methods. Additionally, the pH-gradient that forms indirectly during the bipolar experiment could be considered as further as-
pect of the concept of the corrosion screening method for appropriate materials, such as the aluminium-containing alloys investigated here.
5. Conclusions

In this work, bipolar electrochemistry has been successfully applied in the fields of electrodeposition and corrosion evaluation. In this thesis the applications have been presented in two separate parts, each covering applications related predominantly to one pole of the bipolar electrode at a time.

At the cathode
The feasibility of bipolar electrochemistry for the screening and recycling possibilities for complex metal solutions was investigated. Compositional gradients in some relevant metals could be readily obtained from reference solutions, and to some extent by using dissolved fly ash as the electrolyte. However, the poor spatial resolution of the gradients made straightforward analysis and possibility for separation difficult. The size of the gradient obtained was also found to be highly sensitive to the electrolyte composition. Thus, further optimisation of these systems would be required if they are to be used more effectively, e.g. by combining the approach with extraction methods of different types to change the metal ion composition.

The use of bipolar electrodeposition for creating size gradients in gold nanoparticles tethered to surfaces was also explored. Substrates pre-modified with gold nanoparticles on top of thiolated gold wafers were subjected to external fields in a Au salt-containing solution to obtain gradients in particle size by electrodeposition. The volume of gold deposited along the gradient corresponded well to the predicted current density profile along a bipolar electrode. The approach was also successfully applied to substrates with a pre-fabricated gradient in particle density. This enabled the creation of substrates with simultaneous, orthogonal gradients in both particle size and density. The ability to create substrates with gradients in these properties is highly beneficial for sensor screening applications.

At the anode
The generation of pitting corrosion gradients on stainless steel provided an interesting new approach to study the progression of corrosion damage. The potential gradient across the anodic pole of steel samples acting as bipolar electrodes caused gradual polarisation of the surface. Changes in the feeder current were seen to have a strong influence on the formed gradients. The distribution and morphology of pits across a gradient could, also, be directly
linked with the predicted current density profile across a bipolar electrode. Over short exposure times, pits were observed to initiate further from the anodic edge than would be expected. However, further analysis by the use of a scanning droplet cell (SDC) and HAXPES confirmed a clear gradient in the degree of passivation of the steel surface. These observations provide a valuable contribution to the broader understanding of this method.

A concept for high-throughput array screening was introduced, where a number of samples could be compared for their corrosion properties in the same experiment. The technique was successfully applied for the simultaneous screening of multiple different steel grades. It was found that the relative corrosion resistances of the different grades affected the distribution of the total bipolar current between each sample, in turn affecting the degree of corrosion damage. In principle, this approach could be extended to considerably larger arrays than investigated here.

Finally, two-dimensional gradients in corrosion were achieved by placing samples with a compositional gradient in TiAl, perpendicular to the electric field. The pH change in the electrolyte was also seen to have a strong influence on the sample and the corrosion behaviour of the aluminium in the alloy.

Tying the knots together
From the work presented in this thesis, covering a range of electrochemical processes, we can conclude some general characteristics of bipolar electrochemical experiments. Mainly, this approach was found to be highly sensitive to parameters such as electrolyte composition, cell dimensions and the electrochemistry of the substrate, in strong agreement with the previous literature. However, in both electrodeposition and corrosion screening experiments, it was observed that limitations such as diffusion or passive film formation could significantly affect the current density profile across the bipolar electrode over time; the current density is not necessarily exponential with distance.

The different concepts investigated here demonstrate the versatility of the bipolar approach. In particular, the array and two-dimensional gradient concepts are fascinating directions for future research into high-throughput screening techniques.
6. Outlook

“The ending can never truly be written...”
Rand Miller (Riven)

There are many interesting opportunities to develop the different possible applications of bipolar electrochemistry further. The strategies introduced in this thesis demonstrate the versatility of the technique, especially in electro-deposition and corrosion screening applications. Further development of the different approaches would benefit from, for example:

1. *Operando* studies of the bipolar electrodes utilising different local probe techniques. The possibility to perform measurements, such as the SDC measurements in this work, during the formation of a bipolar gradient would be extremely interesting. Local impedance spectroscopy measurements could also provide new insights into the gradient formation.

2. Corrosion studies on systems other than stainless steel, and continuing the work on different alloys, such as the TiAl alloys investigated here.

3. Exploration of the application of bipolar electrochemistry to other new fields. For example, the approach could be applied to battery research, for example to simultaneously study different stages of lithiation of battery electrodes, or the deposition/stripping behaviour of lithium metal on continuous cycling. The bipolar approach could even be used as a synthetic method, for example to generate solid state batteries in a continuous phase.
Populärvetenskaplig sammanfattning

Det första man tänker på när man hör ordet bipolär är vanligen inte relaterat till kemi eller naturvetenskap, men ordet betyder egentligen inte mer än att något har två poler. I fallet bipolär elektrokemi, eller då man talar om bipolära elektroder, avses helt enkelt att ett objekt agerar både positiv och negativ pol samtidigt. Detta fenomen uppkommer om ett elektriskt ledande föremål utsätts för en yttre drivkraft i form av ett yttre elektriskt fält ($E$) som är tillräckligt starkt för att initiera reaktioner mellan ytan på föremålet och den omgivande lösningen. En del av den totala cell-strömmen kommer då att kunna gå via detta föremål genom oxidation i ena änden, och reduktion i den andra.


Figur 37. a) Gradient i partikelstorlek över en yta modifierad med nanopartiklar. b) Exempel på gropfrätningsgradient genererad genom bipolär elektrokemi.

Den andra delen av arbetet behandlar hur den anodiska sidan kan utnyttjas för att utvärdera korrosionsegenskaper hos material. Fördelen med metoden i det här fallet är att man lätt kan studera olika nivåer av skada på ett och samma prov i ett enda experiment.


Sammansättningsgradier av titan och aluminium utvärderades även i en bipolär uppställning. De två gradienterna placerades vinkelrätt mot varandra så att samtliga sammansättningar kunde utvärderas samtidigt. Efter de bipolära experimenten kunde man tydligt se att den aluminiumrika delen av proverna korroderade mer än den titanrika.

Sammanfattningsvis visade forskningen att strategin att använda bipolär elektrokemi för att generera storleksgradier hos partiklar fungerade mycket väl, liksom möjligheten att utvärdera korrosionsegenskaper hos stål och andra legeringer på ett enkelt sätt. Konceptet kunde även utvidgas till att analysera flera prover samtidigt.
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References


68. Schlumberger, S. New technologies and options for the treatment of flue gas cleaning residues to promote sustainable resource management.


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)