



Universiteit
Leiden
The Netherlands

Cathodic corrosion

Hersbach, T.J.P.

Citation

Hersbach, T. J. P. (2018, December 19). *Cathodic corrosion*. Retrieved from <https://hdl.handle.net/1887/68033>

Version: Not Applicable (or Unknown)

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/68033>

Note: To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden

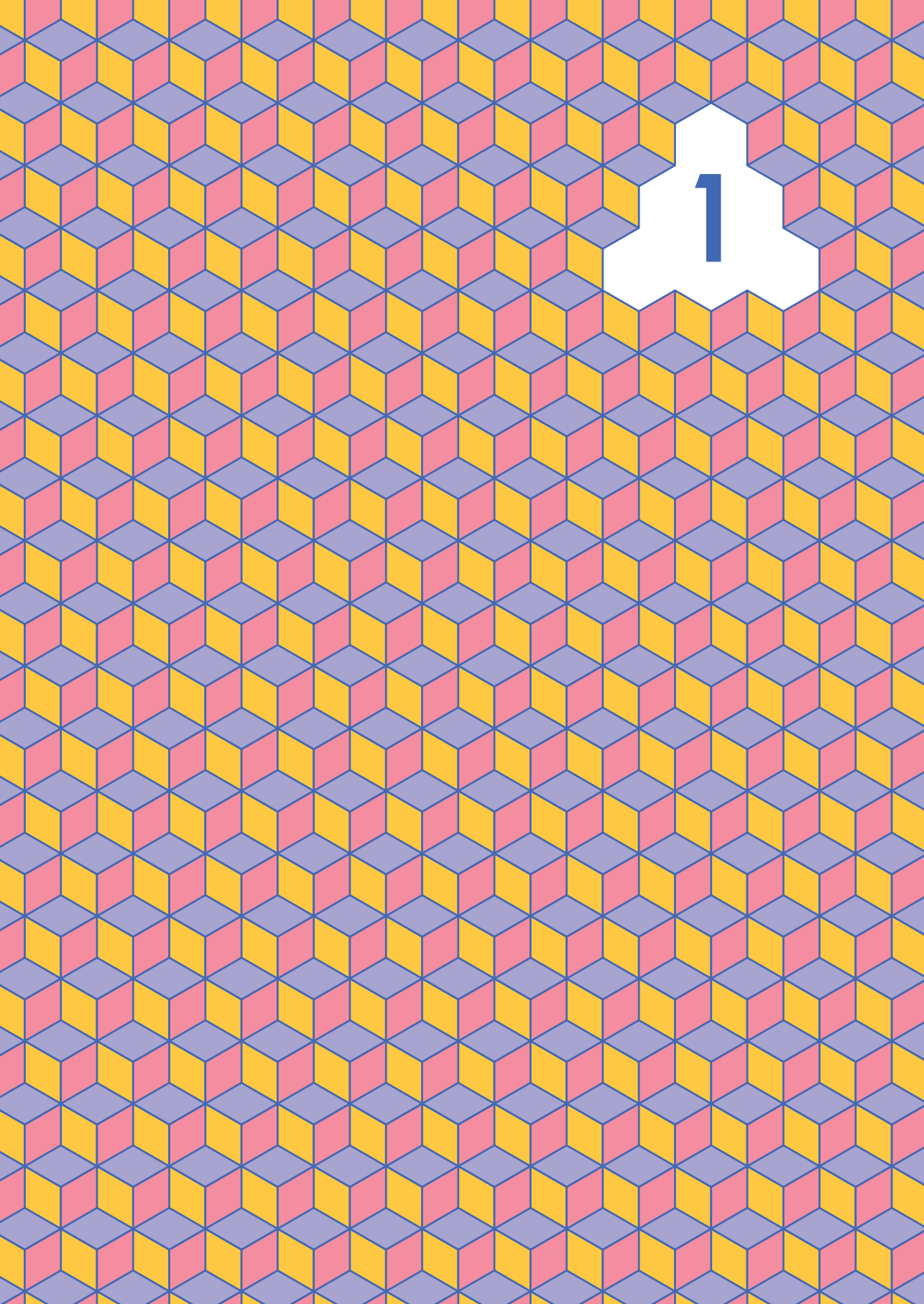


The handle <http://hdl.handle.net/1887/68033> holds various files of this Leiden University dissertation.

Author: Hersbach, T.J.P.

Title: Cathodic corrosion

Issue Date: 2018-12-19



Introduction

1.1 Electrochemistry

Electrochemistry is the scientific discipline that studies the intimate connection between electricity and chemistry.¹ It is the field that enables ever-improving energy storage and conversion by supercapacitors, batteries and fuel cells. It is also the chemical domain that will aid in solving pressing global challenges, like finding CO₂-neutral ways to produce the ammonia that sustains half the world population.² As such, electrochemistry is vital in the current transition from fossil fuels to renewable energy sources.

Electrochemistry uses “electrodes” for conducting experiments. This term either refers to the combination of an electrical conductor and an ionic conductor, or simply to the electrical conductor itself.³ Given the crucial importance of conductors, it can be no surprise that electrochemistry has always made use of metals: the most well-known and ubiquitous electrical conductors. The electrochemical behavior of metals has therefore been studied extensively throughout the past two centuries. A large fraction of these studies has focused on corrosion.

1.2 Corrosion

Corrosion is the electrochemical degradation of a metal that interacts with its environment.³ Most corrosion occurs when metals react with moisture in air. This causes the metal to oxidize (lose electrons) and convert into compounds like metal oxides. Probably the most well-known example of oxidation through corrosion is rusting, in which iron converts to iron oxide. Rusting and related corrosion phenomena can manifest in various ways: rust can form undesired but rather harmless spots on shiny bicycles, but can also cause catastrophic failure of infrastructure like bridges and oil pipelines.

Undesired corrosion has been a problem for centuries. Accordingly, efforts to combat corrosion have been documented since the industrial revolution.⁴ These efforts have generated various methods of corrosion prevention. Some of these methods require chemical modification of either the bulk or the surface of the protected metal; examples include the development of stainless steel and protective coatings. Other methods do not require chemical modification, but instead aim to prevent corrosion through a ‘more electrochemical’ approach. These methods are collectively known as cathodic protection.

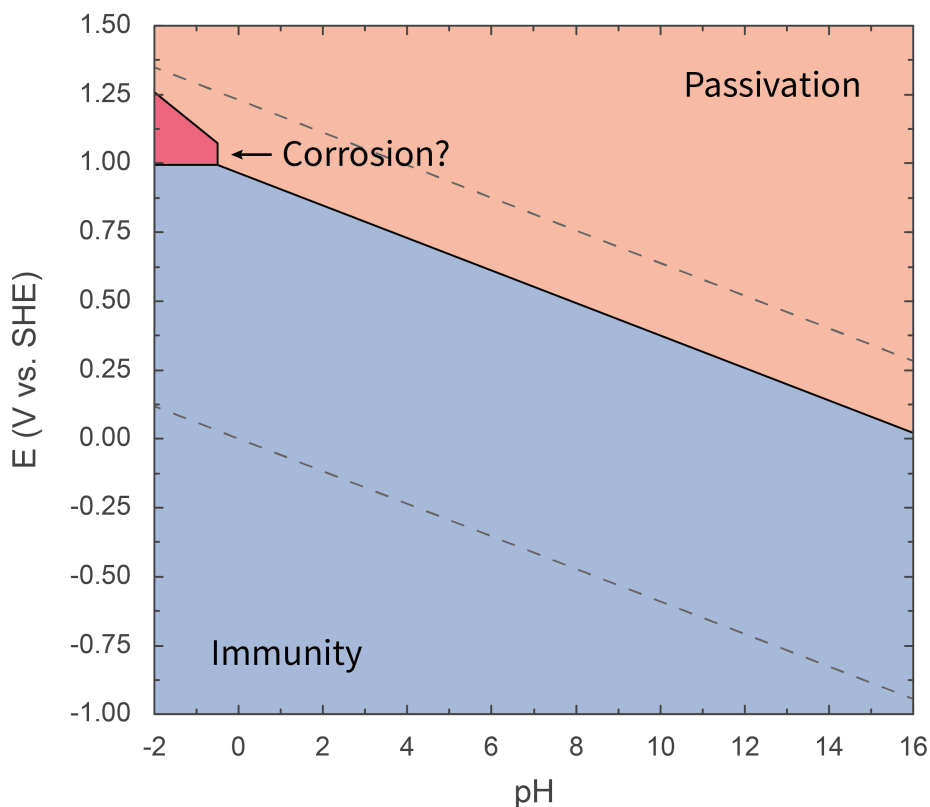


Fig. 1.1 | Simplified Pourbaix diagram for platinum, which indicates whether Pt is expected to corrode at a given combination of electrode potential and solution pH. The dashed grey lines mark the stability window of water; water is thermodynamically stable between the grey lines. This figure is only valid in absence of additional species with which Pt can form compounds. Figure is reproduced from literature.⁵

1.3 Cathodic protection

The invention of cathodic protection is frequently credited to Humphry Davy, a British chemist. Davy studied the corrosion of copper, because, in his words:⁶ *“The rapid decay of the copper sheeting of His Majesty’s ships of war (...) have long attracted the attention of those persons most concerned in the naval interests of the country.”* Through his studies of copper corrosion, Davy discovered that corrosion could be prevented by attaching a small block of zinc to a piece of copper: as long as the ‘noble’ copper and the ‘less noble’

zinc were in electrical contact, the zinc would corrode and protect the copper.

This protective effect of zinc can be perhaps be rationalized most visually with a tool that was invented approximately 150 years after Davy's discovery: the Pourbaix diagram.⁵ Pourbaix diagrams predict the most stable state of an element as a function of its electrochemical potential and the pH of its surrounding electrolyte. An illustrative Pourbaix diagram is shown for platinum in Fig. 1.1. This diagram is simplified and simply illustrates whether platinum is expected to corrode.

The diagram is divided into a red/orange region at higher potentials and a blue region at lower potentials. In the red/orange region, platinum oxidizes. For platinum, such oxidation generally leads to a protective platinum oxide layer on the electrode. This layer significantly slows down corrosion and the platinum is considered 'passivated'. If this passivating layer does not form, the platinum corrodes, as is shown in red in Fig. 1.1. Similar diagrams can be drawn for other metals. Many of those, like iron and copper, contain large areas where the metal corrodes.

Corrosion can be prevented by moving the electrochemical potential of the protected metal into the blue region of the diagram. This was achieved by Davy's block of zinc, which gives up electrons rather easily and therefore has a low electrochemical potential. Alternatively, one can lower a metal's electrochemical potential by connecting it to an electrical power source. Though this approach differs from Davy's original method, it similarly immunizes a metal to corrosion by moving it into the blue region in the Pourbaix diagram.

One might interpret the Pourbaix diagram to mean that metallic platinum is stable at any potential marked in blue. After all, these potentials are too negative to oxidize platinum. However, the absence of oxidation only implies immunity to conventional *anodic* corrosion. Platinum can still corrode at low potentials, through an enigmatic process known as *cathodic* corrosion. Cathodic corrosion is the focus of this thesis.

1.4 Cathodic corrosion

Cathodic corrosion was first described around 1900 by Fritz Haber,^{7,8*} who observed the formation of large clouds of dust from cathodically (negatively) polarized metals. Haber

* Though cathodic corrosion is generally not included in Pourbaix diagrams, Pourbaix was likely aware of Haber's work; Haber's article on the cathodic decomposition of platinum is briefly mentioned in Pourbaix' 1974 *Atlas of Electrochemical Equilibria*.

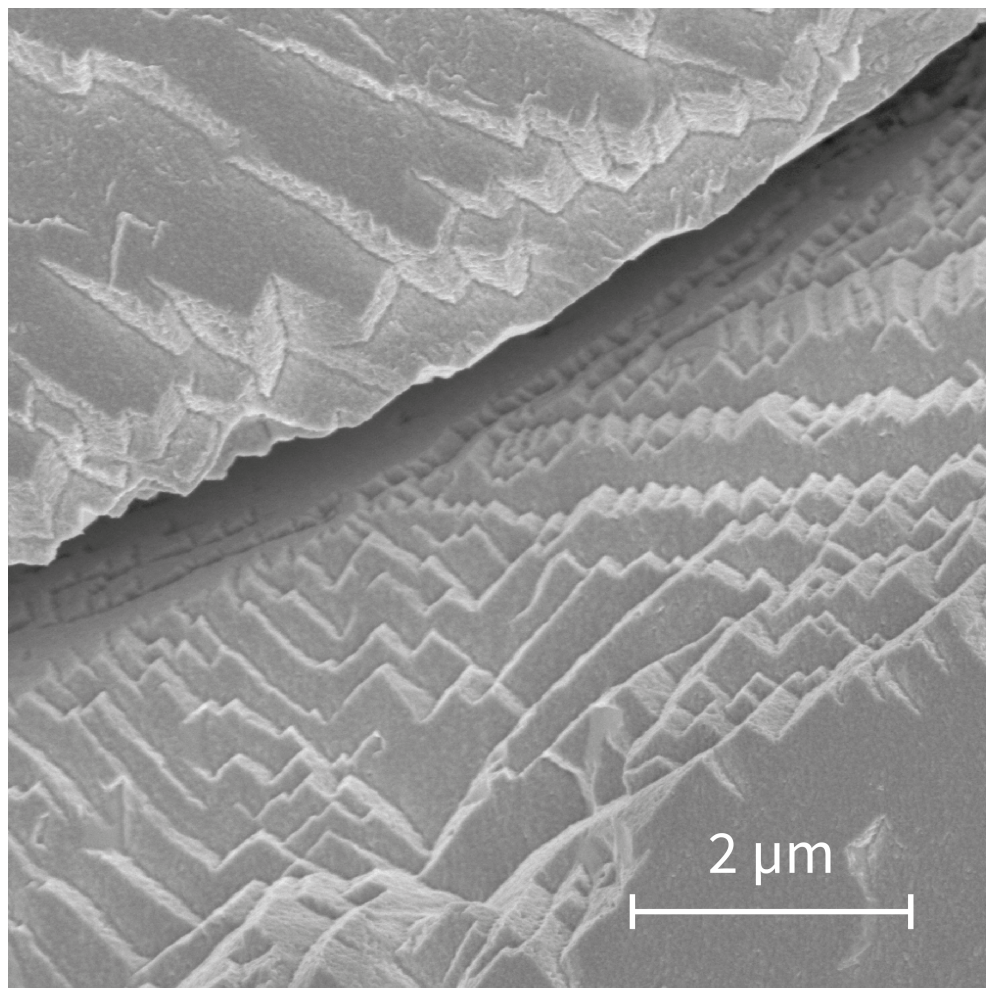


Fig. 1.2 | Scanning electron micrograph of a cathodically corroded platinum electrode. The image features a boundary between two crystal grains, on which etching produced large geometrical patterns. Etching was performed in 5 *M* NaOH, by applying a 0.5 *Hz* square wave with potential limits of -1.0 V and 2.0 V versus the reversible hydrogen electrode for 2 minutes.

ascribed these metallic dust clouds to the formation and subsequent destruction of alloys of the corroded metal and cations like Na^+ and K^+ in the working solution. This appeared to explain cathodic corrosion and interest in the phenomenon vanished as quickly as it appeared; cathodic corrosion was briefly studied in the 1960s and 1970s,⁹ but remained generally un-explored in the 20th century.

Cathodic corrosion re-emerged as a topic of interest around 2009, when it was used

to create metallic nanoparticles.^{10–12} This nanoparticle production method involves both cathodic and anodic corrosion, which are combined by applying an alternating current (AC) potential to a metallic electrode. This AC profile rapidly switches between positive (anodic) and negative (cathodic) potentials, which quickly produce a cloud of nanoparticles. These nanoparticles leave behind a dramatically etched metallic electrode, as is illustrated in Fig. 1.2.

Though these results re-ignited the interest in cathodic corrosion, they either invoked anodic corrosion as the cause of nanoparticle formation,^{10,11} or referenced Haber's hypothesis of cation alloying.¹² Both explanations were disproven by work from Yanson *et al.* in 2011.¹³ This work conclusively established cathodic corrosion as driving the nanoparticle formation and ruled out the creation and destruction of alkali metal alloys. Instead, an entirely new reaction mechanism was proposed.¹³

This hypothetical mechanism is illustrated in Fig. 1.3.[†] It takes into account that cathodic corrosion occurs at potentials where hydrogen evolution occurs. Due to this vigorous hydrogen production, the working solution near the platinum surface is presumably depleted from 'free water'. This means that all water is either solvating the working electrolyte (NaOH in this example), or is converted into H_2 and OH^- upon contact with the platinum electrode. The electrode itself is covered in adsorbed hydrogen and cations like Na^+ (Panel 1).

Under these conditions, atoms from the electrode surface are then thought to convert into "metallic anions" (Panel 2). The exact nature of these anions is unknown, but there is strong evidence that they are stabilized by non-reducible cations: without the presence of cations like Na^+ , cathodic corrosion does not take place.¹³ After corrosion forms the cation-stabilized anionic species, this species dissolves into the working solution and moves away from the electrode.

The anion rapidly encounters free water (Panel 3). Upon contact, the ion is oxidized back to its metallic form by the water, which in turn decomposes into H_2 and OH^- . This metallic platinum then diffuses around the working solution. It either finds the original platinum surface and re-deposits or it finds other platinum atoms and nucleates to form a nanoparticle (Panel 4).

At the time of writing this thesis, this is the only reaction mechanism that is consis-

[†] Though this figure illustrates the initial hypothesized reaction mechanism, it contains several elements that reflect the improved understanding gained in this thesis.

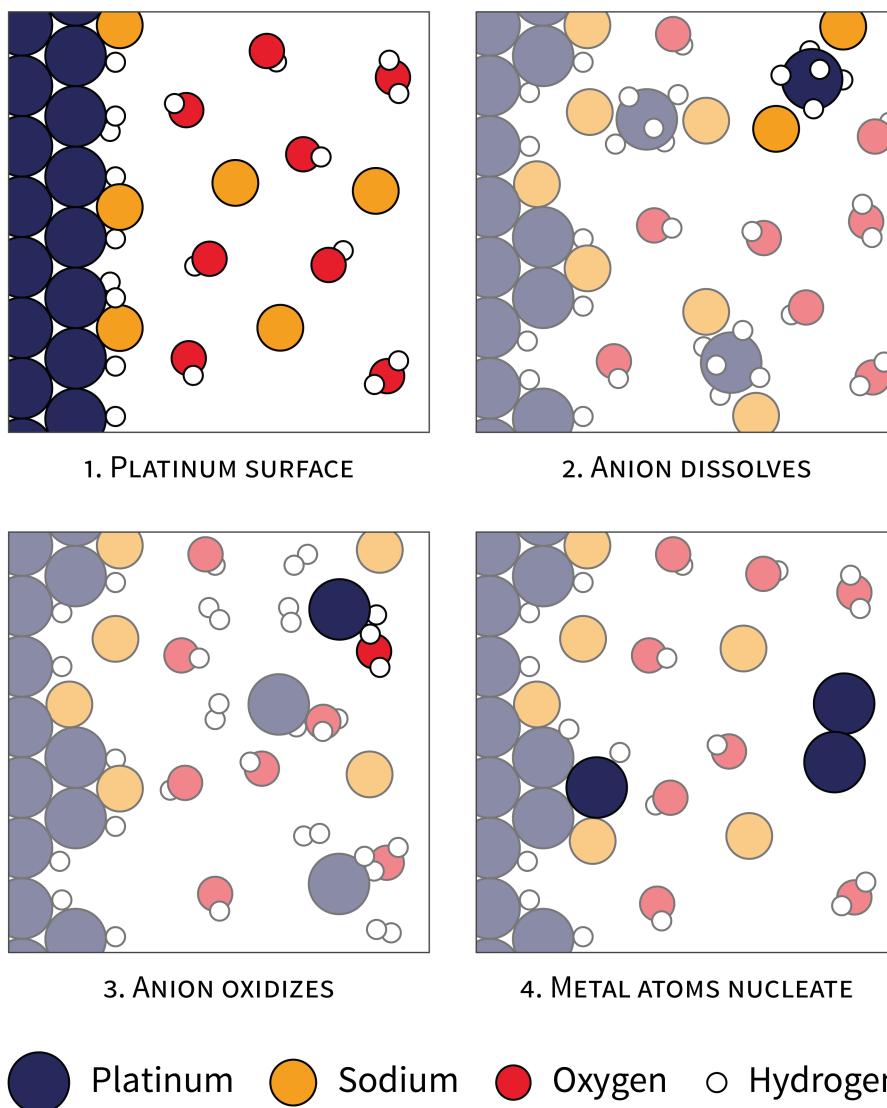


Fig. 1.3 | Illustration of the hypothesized cathodic corrosion mechanism, using Pt as an example. This corrosion occurs at potentials where the platinum is covered by adsorbed hydrogen and cations like Na^+ (Panel 1). At these potentials, hydrogen evolution occurs as well. Under these conditions, some Pt converts into an unknown cation-stabilized anion (Panel 2), which dissolves. (The anion might consist of more than one platinum atom.) Eventually, the anion encounters water and is oxidized back to atomic platinum (Panel 3). This platinum can then redeposit on the electrode or nucleate into nanoparticles (Panel 4).

tent with all experimental observations. However, this hypothesized mechanism presents several crucial questions. Perhaps most importantly, what is the exact nature of the mysterious anion? Is it, like originally suggested, a metallic anion or is it a compound containing other atoms? Furthermore, what causes the large, well-defined geometric patterns like those in Fig. 1.2? How do different metals and their alloys behave during cathodic corrosion? And could cathodic corrosion be used for more than just nanoparticle production?

1.5 Outline of this thesis

This thesis aims to answer the abovementioned questions regarding cathodic corrosion. In doing so, emphasis will be placed on well-defined systems. Most chapters will therefore use reference electrodes and exclude the occurrence of anodic corrosion. These two factors restrict the production of practical amounts of nanoparticles. Most of the work will therefore not focus on nanoparticles, but will instead mainly study the surfaces that are affected by cathodic corrosion. These surfaces will consist of Pt, Rh and Au, which can conveniently be characterized electrochemically.

Taking into account these considerations, this thesis contains six experimental chapters. These chapters can loosely be divided into four ‘fundamental’ chapters (Chapter 2–5) and two ‘applied’ chapters (Chapter 6–7).

As the first fundamental chapter, Chapter 2 establishes the experimental protocol that will be followed in the following four chapters. This protocol combines cyclic voltammetry and scanning electron microscopy to study corroded Pt electrodes. These techniques are used to establish the onset of cathodic corrosion in 10 *M* NaOH. In addition, these methods reveal a strong preference for forming (100)-type sites on the surface, which correspond to the formation of geometric etch pits. This preference is hypothesized to be caused by Na⁺ adsorption during cathodic corrosion.

Chapter 3 expands on these observations by studying the corrosion onset potential and etching preference for both Rh and Au. These metals are more challenging to handle, because of their constraints in electrode preparation. Nonetheless, Chapter 3 identifies both onset potentials and etching preferences for Rh and Au. Au differs from Pt and Rh, because it prefers forming (111) sites. This difference is tentatively explained by a difference in Na⁺ adsorption on these metals, as will be supported by density functional theory (DFT) calculations of sodium adsorption.

Then, Chapter 4 closely examines the role of cations in determining both the onset potential and etching preference of cathodic corrosion. This examination relies on systematically studying the etching behavior of Pt, Rh and Au in solutions of LiOH, NaOH and KOH. These experiments reveal that cations indeed play a strong role in controlling cathodic corrosion. The experiments are supported by DFT calculations of cation adsorption, including the effects of solvation. Though the DFT calculations cannot quantify the exact role of cations, they do indicate that cations are adsorbed during cathodic corrosion. An equally important role is suggested for adsorbed hydrogen by additional theoretical calculations. Based on the importance of both adsorbed cations and hydrogen, Chapter 4 will suggest that the anionic cathodic corrosion intermediate is a ternary metal hydride.

The formation of ternary metal hydrides will be explored in Chapter 5. In this chapter, Pt is studied during corrosion with X-ray absorption spectroscopy (XAS). Through XAS, small changes in the chemical state of Pt are observed during cathodic corrosion. These changes are quantified through peak fitting and creating difference X-ray absorption spectra. This analysis is supported by using first-principles calculations to simulate spectra for ternary metal hydrides. One hydride, Na_2PtH_6 , generates simulated spectra that closely match the experimental spectra. Na_2PtH_6 is therefore the most likely species underlying the cathodic corrosion of platinum.

Following these fundamental insights, the last two chapters will focus on applying cathodic corrosion. The first of these chapters is Chapter 6. This chapter uses the insights from Chapter 2 and 4 to optimize a Pt(111) single crystal for catalyzing the oxygen reduction reaction (ORR). Specifically, the Pt(111) electrode is mildly corroded cathodically, which creates optimal sites for ORR catalysis.

Finally, Chapter 7 concerns the creation of Pt, $\text{Pt}_{55}\text{Rh}_{45}$, $\text{Pt}_{12}\text{Rh}_{88}$ and Rh nanoparticles through combining cathodic and anodic corrosion. Pure and alloyed nanoparticles are created for various cathodic and anodic potential limits in the applied AC protocol. These variations generate insights into the relative roles of cathodic and anodic corrosion in nanoparticle production. The produced nanoparticles are then subjected to structural and compositional analysis by X-ray diffraction, X-ray absorption spectroscopy and transmission electron microscopy. This multifaceted analysis reveals small degrees of elemental segregation in the nanoparticles.

Combined, these chapters generate an improved understanding of cathodic corrosion. They provide a detailed impression of the etching behavior of Pt, Rh and Au during

purely cathodic corrosion. Perhaps most importantly, this understanding provides concrete indications for the existence of Na_2PtH_6 during cathodic corrosion. If correct, this would be the first reported case of ternary metal hydrides in aqueous media.

The chapters also facilitate the application of cathodic corrosion. Chapter 4 provides concrete guidelines for structuring metallic electrodes through cathodic corrosion. The implications of such structuring on catalysis are then illustrated in Chapter 6. Adding Chapter 7, the thesis ends with additional recommendations on nanoparticle production through cathodic corrosion.

As such, the present thesis marks a significant improvement in both the knowledge of cathodic corrosion and the prospects for using this unique phenomenon to tackle the electrochemical challenges of the 21st century.

References

1. Bard, A. J. & Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications* 2nd ed. (Wiley, New York, 2001).
2. Erisman, J. W., Sutton, M. A., Galloway, J., Klimont, Z. & Winiwarter, W. How a century of ammonia synthesis changed the world. *Nature Geoscience* **1**, 636–639 (2008).
3. Bard, A. J., Inzelt, G. & Scholz, F. *Electrochemical Dictionary* 2nd ed. (eds Bard, A. J., Inzelt, G. & Scholz, F.) (Springer Berlin, Heidelberg, 2012).
4. Sato, N. in *Green Corrosion Chemistry and Engineering* (ed Sharma, S. K.) 1–32 (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011).
5. Pourbaix, M. *Atlas of electrochemical equilibria in aqueous solutions* 2nd ed., 644 (National Association of Corrosion Engineers, 1974).
6. Davy, H. On the Corrosion of Copper Sheeting by Sea Water, and on Methods of Preventing This Effect; And on Their Application to Ships of War and Other Ships. *Philosophical Transactions of the Royal Society of London* **114**, 151–158 (1824).
7. Haber, F. Über Elektrolyse der Salzsäure nebst Mitteilungen über kathodische Formation von Blei. III. Mitteilung. *Zeitschrift für anorganische Chemie* **16**, 438–449 (1898).
8. Haber, F. The Phenomenon of the Formation of Metallic Dust from Cathodes. *Transactions of the American Electrochemical Society* **2**, 189–196 (1902).
9. Kabanov, B. N., Astakhov, I. I. & Kiseleva, I. G. Formation of crystalline intermetallic compounds and solid solutions in electrochemical incorporation of metals into cathodes. *Electrochimica Acta* **24**, 167–171 (1979).
10. Huang, W., Chen, S., Zheng, J. & Li, Z. Facile preparation of Pt hydrosols by dispersing bulk Pt with potential perturbations. *Electrochemistry Communications* **11**, 469–472 (2009).
11. Liu, J., Huang, W., Chen, S. & Hu, S. Facile electrochemical dispersion of bulk Rh into hydrosols. *Int. J. Electrochem. Sci.* **4**, 1302–1308 (2009).
12. Leontyev, I., Kuriganova, A., Kudryavtsev, Y., Dkhil, B. & Smirnova, N. New life of a forgotten method: Electrochemical route toward highly efficient Pt/C catalysts for low-temperature fuel cells. *Applied Catalysis A: General* **431–432**, 120–125 (2012).
13. Yanson, A. I. et al. Cathodic Corrosion: A Quick, Clean, and Versatile Method for the Synthesis of Metallic Nanoparticles. *Angewandte Chemie International Edition* **50**, 6346–6350 (2011).