Platinum electrochemistry through a magnifying glass

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1 Introduction

During a chemical reaction, reactant molecules need to encounter each other at exactly the right place, at the right time, and with the right orientation. As a result, many bulk reactions occur only at extremely low rates. Adding energy to the system, typically in the form of heat or pressure, leads to increased reaction rates. However, most of this energy is used to overcome the so-called reaction barrier (see Fig. 1.1), and is therefore not used efficiently. Catalysts provide a much more effective pathway to store and release chemical energy.[1] A perfect catalyst binds reactant molecules in a way that is optimal for the reaction of interest to occur, such that the reaction barrier is as low as possible. This does not only increase the rate of product formation (the activity), but by choosing the right catalyst and operating conditions, one can also influence which product is formed (the selectivity). Catalysts are generally considered to be regenerated at the end of the catalytic cycle, or even to remain unaltered during the reaction. In this way, a single catalyst could be used indefinitely without ever being consumed.

Catalysts play a prominent role in the production processes of approximately 90% of all our chemicals and materials.[2] As such, they have a huge impact on our society, although most people are unaware of this. Most large-scale industrial processes make use of heterogeneous catalysis, in which the catalyst is in a different phase (typically solid) than the reactants (gas or liquid). Unfortunately, it turns out that most catalysts do not exhibit the ideal textbook behavior. Although reaction barriers are decreased (see Fig. 1.1) and a single catalyst remains active for many catalytic cycles, the input of additional energy and 'fresh' catalyst material are still required. The implications of these phenomena at the industrial scale can not be overestimated. For example, the synthesis of ammonia (the key step in the production of artificial fertilizers) consumes more than 1% of the global energy supply.[3] The production of gasoline from otherwise unusable fractions of crude oil (using fluid catalytic cracking) consumes approximately 2300 tons of catalyst per day.[4] With this in mind, it comes at no surprise that many research efforts in catalysis focus on the development of catalysts that exhibit both increased reactivity and stability.

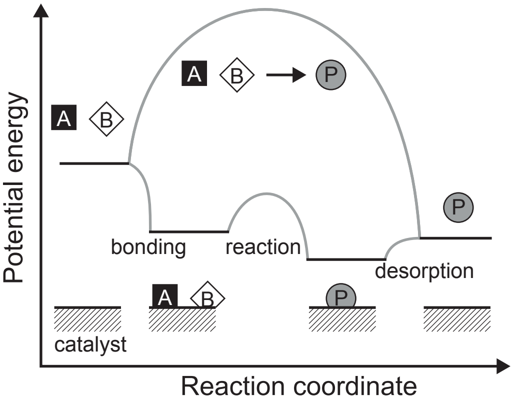

Fig. 1.1 | Potential energy diagram: Schematic overview of the energy needed for a chemical reaction to occur with and without a catalyst present. Figure adapted from Ref. [5].

The source of the input energy provides another important reason to study catalysis. Since the industrial revolution, energy is largely generated by the combustion of fossil fuels. However, the supply of fossil fuels is limited and often dependent on politically unstable regions. Furthermore, the emission of CO_2 into the atmosphere is the main contributor to anthropogenic global warming.[6] In recent years, more and more people have realized that fossil fuels are not suitable as energy source for a modern society and that we need to switch to more sustainable alternatives. The main energy source of the future will be the sun; directly via solar panels, and/or indirectly for example using wind turbines. This implies that energy supply will be in the form of electricity, which makes one wonder about possibilities to use this electricity in a direct way to drive chemical reactions. The reverse process of converting chemical energy into electricity is of interest to make electricity available when and where it is required. Electrochemistry is the field that considers these challenges.

1.1 Electrochemistry

Large scale industrial applications of electrochemistry are found in the production of chlorine gas (chloralkali process), the production of aluminum (Hall-Héroult process), and electroplating.[7,8] Closer to home, electrochemistry is applied in batteries when portability is important and the energy consumption is relatively low and short. Interestingly, the very first electric 'cars' were already constructed in the first half of the 19th century, although they were soon outcompeted by combustion engines.[9] With the improvement of technology during the last centuries, the application of electrochemistry for mobility has gained renewed interest. A promising approach, besides using stored charge from a battery, is to convert external fuels into electricity using a fuel cell. The most obvious fuel for such a device would be hydrogen,[10] but also other chemicals with a high energy-density, like methanol[11] and hydrazine,[12] are used in some applications.

Figure 1.2 shows a schematic overview of a hydrogen fuel cell. At one of the electrodes, the hydrogen gas is oxidized to form protons and electrons (Reaction 1.1). The protons diffuse through the electrolyte to the other electrode, whereas the electrons will move through the external electric circuit. At the other electrode, the protons and electrons are consumed to reduce molecular oxygen, forming water (Reaction 1.2). Thus, the overall reaction becomes:

$$\mathrm{H_2} \longrightarrow 2\ \mathrm{H^+} + 2\ \mathrm{e^-} \qquad E^{\ominus} = 0\ V \tag{1.1}$$

$$\tfrac{1}{2}\,\mathrm{O_2} + 2\ \mathrm{H^+} + 2\ \mathrm{e^-} \longrightarrow \mathrm{H_2O} \qquad E^{\ominus} = 1.23\ V \qquad (+) \tag{1.2}$$

$$\mathrm{H_2} + \tfrac{1}{2}\,\mathrm{O_2} \longrightarrow \mathrm{H_2O} \qquad E_{cell} = 1.23\ V \tag{1.3}$$

which should deliver a potential of 1.23 V. If a potential above 1.23 V is applied between the electrodes, as is done in an electrolyzer, the reaction is reversed. One of the most suitable catalyst materials for both reactions is platinum.[13] However, even with a platinum catalyst, significant amounts of energy are lost during the reduction/formation of oxygen. Moreover, the electrodes used in this reaction tend to degrade over time. Fundamental studies providing insight in these processes are necessary to boost the application of this sustainable energy technology.

To study electrocatalysts, the overall electrochemical process (Reaction 1.3) is separated into the reactions occurring at the two different electrodes, so-called half-reactions (Reactions 1.1 and 1.2). The electrode that is studied is the working electrode and its potential is controlled with respect to a reference electrode by a potentiostat. A counter electrode delivers the current necessary to close the electronic circuit. The most common electrochemical experiment is to scan the potential of the working electrode and record the resulting current; a (cyclic) voltammogram. By combining results from different experiments, the electrochemical current can be related to the (half-)reactions occurring at the working electrode.

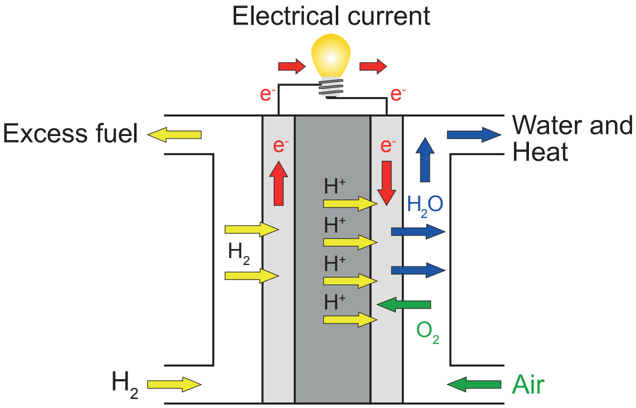

Fig. 1.2 | Hydrogen fuel cell: Schematic overview of a fuel cell that converts H_2 and O_2 into electricity and water. Figure adapted from Ref. [5].

1.2 Model catalysts

Heterogeneous catalysts are only active where they come into contact with reactants, i.e. the surface. To use the (often expensive) catalyst material in an optimal way, one should therefore maximize the surface to volume ratio. Thus, a typical application will contain large number of electrocatalytically active nanoparticles, deposited on a porous, conducting support. Zooming in on a typical nanoparticle (see Fig. 1.3A), it becomes clear that its surface is composed of a wide variety of atomic arrangements. One can distinguish different kinds of facets that are connected via edge and corner sites. It turns out that not only the material, but also these specific arrangements have a large influence on the catalytic activity.[14]

To study the relationship between the atomic surface structure and the electrochemical reactivity, it is most convenient to make use of well-defined (single crystalline) model samples containing only a few different surface geometries. Combining the data from different samples ultimately delivers the reactivity of single surface sites. Figure 1.3 provides several examples of different surface structures. These surfaces can be classified according to the orientation of the surface plane with respect to the smallest repetitive unit (unit cell) of the bulk material. This orientation is referred to as a Miller index. Figure 1.3B shows the three most densely packed facet geometries: the (111)* surface with a hexagonal unit cell; the

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* In the Miller index notation, () indicate specific surface planes and {} indicate families of equivalent surface planes.

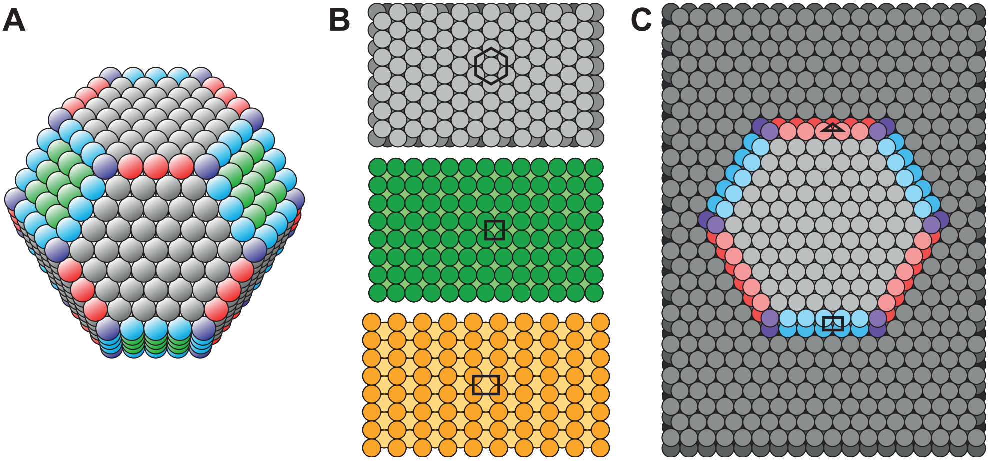

Fig. 1.3 | Atomic scale surface structures: (A) A model nanoparticle containing different facet-, edge-, and corner-sites. Figure by Richard van Lent. **(B)** The three most densely packed surface structures, from top to bottom: (111), (100), and (110). **(C)** Adatom island on an (111) surface containing {100} (blue) and {111} (red) type step edges separated by corner sites.

(100) surface with a square unit cell; and the (110) surface with a rectangular unit cell. Figure 1.3C shows an example of an adatom island on a (111) terrace, leading to the formation of step edges. These edges themselves also exhibit different geometries, as shown here for the {100} (blue) and {111} (red) step edges.

Although single crystal experiments provide detailed information on structure-activity relationships, it is difficult to apply this information directly in a real application. An approach to bridge this gap is by studying only small parts of a heterogeneous (polycrystalline) sample at a time. Experimental techniques to perform such experiments are discussed in the next section.

Since it was discovered that (single crystalline) platinum electrodes can relatively easy be prepared by flame-annealing, the knowledge of their fundamental electrochemical properties has drastically improved.[15] However, there are still open questions considering electrode degradation processes and structure-activity relationships. To answer these questions, one cannot rely on electrochemical experiments alone. Information on the electrode surface structure, preferably within the electrochemical cell (*in situ*) or even during the reaction (*operando*), is of crucial importance. Various experimental techniques have been developed to reach this goal, each with their own specific advantages and drawbacks. The techniques used in this thesis are part of the ‘electrochemical scanning probe microscopy’ techniques (EC-SPM). They make use of a physical probe that is scanned across the electrode to visualize its structure and/or activity at the nano- to micrometer length scale.

1.3 Electrochemical scanning probe microscopy

The fast development of scanning probe techniques since the 1980s opened up complete new research fields to directly study interfacial processes.[16,17] Although many different approaches are available, there are three techniques that are of special interest within the scope of this thesis. These techniques are electrochemical scanning tunneling microscopy (EC-STM), scanning electrochemical microscopy (SECM), and scanning electrochemical cell microscopy (SECCM). An overview of these techniques is provided here, but the interested reader is referred to various textbooks and reviews that are available in the literature.[18–21]

In STM, a sharp metallic tip is brought at a close distance (a few Å) to a conductive sample. When a bias voltage is applied, electrons will tunnel through the gap in between the tip and sample electrodes. As the tunneling probability depends exponentially on the tip-to-sample distance, STM exhibits a height resolution down to 0.01 nm. Scanning the tip across the surface while maintaining a constant tunneling current or constant tip height, generates an image of the local surface structure.[*] The maximum lateral resolution is slightly lower than the height resolution, but still on the subatomic scale, routinely leading to atomically resolved images.

The working principle of an STM can also be applied under electrochemical conditions, although this leads to some experimental complications. However, the added value of directly visualizing electrode structures under (reactive) electrochemical conditions makes it worthwhile to meet these challenges. Most importantly, one has to realize that the sample and tip currents no longer just depend on the tip-to-sample distance and the bias voltage, but also on the electrochemical conditions. Reactions occurring at either of these electrodes lead to additional electrochemical (faradaic) currents, which interfere with the imaging experiment. To minimize the faradaic contribution to the tunneling current, the tip electrode

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[*] The image represents the ‘local density of electronic states’, which for a homogeneous sample can be considered equivalent to the surface structure.

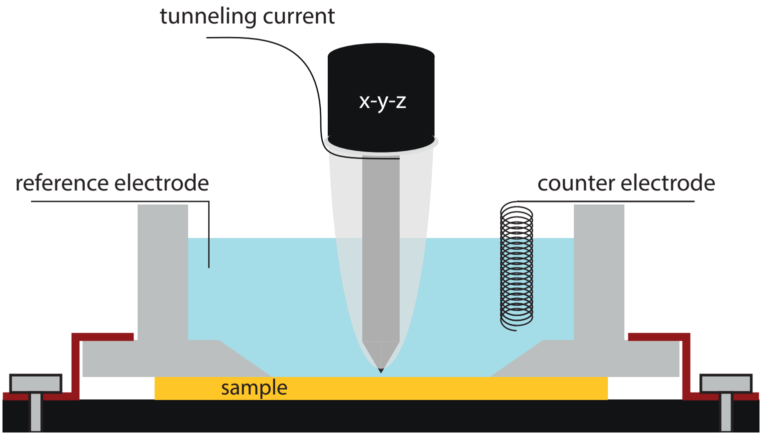

Fig. 1.4 | EC-STM cell: Schematic overview of the EC-STM cell. The sample and cell are clamped down onto a baseplate. The electrochemical current is recorded via the sample, the tunneling current via the tip. All potentials are controlled using a bipotentiostat.

is coated with a non-conductive material leaving only the very apex exposed. The stability of the tip material should also be considered. Tungsten is widely used to prepare STM tips for vacuum experiments because of its mechanical properties and because it is easily etched into sharp tips. In EC-STM, a PtIr alloy is commonly applied. Finally, one should realize that in EC-STM the potentials of the tip and the sample have to be controlled individually (using a bipotentiostat), whereas otherwise only the bias voltage has to be controlled. A schematic overview of the EC-STM cell is shown in Fig. 1.4.

Scanning electrochemical microscopy (SECM), like EC-STM, also makes use of a small metallic tip that is scanned across the sample surface. A typical tip consists of a disk electrode with a radius of a few micrometers down to a few nanometers (ultramicroelecrode, UME). This tip is scanned across the sample at a distance that is similar to its radius. The tip signal originates from an electrochemical current that occurs at the UME surface. As a result, the spatial resolution is on the order of the dimensions of the used tip. The highest resolution reported so far is about 1 nm, although these results are expected to be affected by a tunneling current.[22,23] The current-distance relationship depends on the nature of the sample and the SECM operating mode. The most common mode is the feedback mode, where products formed at the sample react at the UME, leading to an increased UME current for decreasing distance. SECM is a flexible technique to image micrometer-resolved electrochemical activity and is applied in a wide range of research areas from catalyst screening to imaging of living cells.

A disadvantage of standard SECM modes is that the electrochemical signal is convoluted with the topographical information. In the feedback mode, for example, it is not directly clear if an increase in the UME current results from a catalytically more active part of the sample or from a decreased tip-to-sample distance. One way to circumvent this problem is by using scanning electrochemical cell microscopy, schematically illustrated in Fig. 1.5.

In SECCM, the probe is not a metallic electrode, but a double-barrel quartz capillary filled with electrolyte. At the apex of the capillary, an electrolyte droplet is formed which defines the electrochemical cell. Only those parts of the sample that are in contact with this droplet will contribute to the overall faradaic signal, as the rest of the sample remains exposed to a gas atmosphere. In this way, the local electrochemical activity (via the sample) can be measured simultaneously with the electrode topography (via additional electrodes in both barrels of the capillary). As in SECM, the spatial resolution is mainly determined by the dimensions of the used probe and chosen according to the studied sample. These probes can be reproducibly fabricated with diameters ranging from a few micrometers to tens of nanometers. In addition, SECCM is easily combined with other techniques to characterize the sample in more detail.

1.4 Outline of this thesis

The main goal of this thesis is to study fundamental platinum electrochemistry, making use of EC-SPM techniques. Chapters 2 and 3 use EC-STM to study the degradation of a Pt(111) electrode upon the application of oxidation-reduction cycles. In this process we observe the formation of Pt nanoislands all over the atomically flat surface. Chapter 2 describes the evolution of the overall roughness of the electrode and correlates this to its total electrochemical signal. From this analysis we identify two different growth regimes: a ‘nucleation & early growth’ regime of nanoisland formation, and a ‘late growth’ regime after island coalescence. In Chapter 3, the EC-STM data are analyzed in more detail to correlate the evolution of individual surface site densities to the complex evolution of the voltammetric signal. Here, we disentangle the electrochemical signal of individual step-, facet-, and vacancy-sites.

Chapter 4 describes a new mode of SECCM, in which a full electrochemical measurement can be made at each position of the surface. This voltammetric

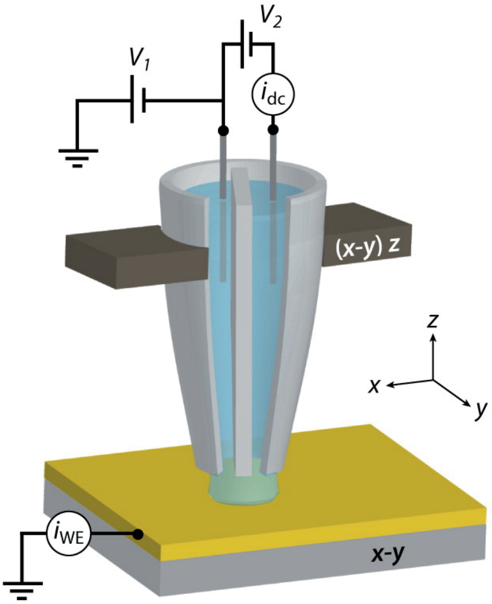

Fig. 1.5 | SECCM setup: Schematic overview of the SECCM technique. The electrochemical cell is defined by the droplet at the apex of the capillary. The faradaic current is measured at the sample. The current between the two electrodes in the capillary provides the topographical information. The potential of the working electrode is controlled by the offset (V_1) and bias (V_2) voltages, applied via the capillary using a bipotentiostat. Figure reproduced from Ref. [21]

SECCM mode is used to study the oxidation of hydrazine at a polycrystalline platinum electrode. We demonstrate that voltammetric SECCM is able to visualize differences in activity that are related to the (average) local surface structure. Additionally, it is shown that the reactivity is dramatically decreased in the presence of oxygen, which is ascribed to the presence of a nonfaradaic hydrazine oxidation pathway.

Chapter 5 describes the electrochemical reactivity of platinum ultramicroelectrodes. UMEs are not only used as SECM tips, but also in many other catalytic studies to overcome limitations due to reactant diffusion or electrolyte resistance. However, they cannot be cleaned by flame-annealing and many studies using UMEs do not provide any information on the cleanliness of the UME surface. By comparing the reactivity of UMEs to that of flame-annealed electrodes, it is shown that UMEs exhibit a decreased reactivity towards surface sensitive reactions. The limited possibilities to clean UMEs are argued to cause these observations.

References

1. Niemantsverdriet, J. *Spectroscopy in Catalysis: An Introduction* (Wiley, 2008).
2. Bowker, M. *The basis and applications of heterogeneous catalysis* (Oxford University Press, Incorporated, 1998).
3. International Fertilizer Association. *Energy Efficiency and CO_2 Emissions in Ammonia Production* tech. rep. (2009), 4.
4. Vogt, E. T. C. & Weckhuysen, B. M. Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis. *Chem. Soc. Rev.* **44,** 7342–7370 (20 2015).
5. Den Dunnen, A. *Surface-structure dependencies in catalytic reactions* PhD thesis (Leiden University, 2015), 2.
6. Davis, S. J., Caldeira, K. & Matthews, H. D. Future CO_2 Emissions and Climate Change from Existing Energy Infrastructure. *Science* **329,** 1330–1333 (2010).
7. Botte, G. G. Electrochemical Manufacturing in the Chemical Industry. *Electrochem. Soc. Interface* **23,** 49–55 (3 2014).
8. Schlesinger, M. & Paunovic, M. *Modern Electroplating* (Wiley, 2011).
9. Guarnieri, M. *Looking back to electric cars* in *History of Electrotechnology Conference* (IEEE, 2012), 1–6.
10. Hydrogen on the rise. *Nature Energy* **1,** 16127 (2016).
11. Hamnett, A. in *Handbook of Fuel Cells* (John Wiley & Sons, Ltd, Chichester, UK, 2010).
12. Kohnke, H. in *Handbook of Fuel Cells* (John Wiley & Sons, Ltd, Chichester, UK, 2010).
13. Holton, O. T. & Stevenson, J. W. The Role of Platinum in Proton Exchange Membrane Fuel Cells. *Platinum Metals Rev* **57,** 259–271 (2013).
14. Koper, M. T. M. Structure sensitivity and nanoscale effects in electrocatalysis. *Nanoscale* **3,** 2054–2073 (2011).
15. Climent, V. & Feliu, J. M. Thirty years of platinum single crystal electrochemistry. *J. Solid State Electrochem.* **15,** 1297–1315 (2011).
16. Binnig, G., Rohrer, H., Gerber, C. & Weibel, E. Surface Studies by Scanning Tunneling Microscopy. *Phys. Rev. Lett.* **49,** 57–61 (1 1982).
17. Bard, A. J., Fan, F. R. F., Kwak, J. & Lev, O. Scanning Electrochemical Microscopy. Introduction and Principles. *Anal. Chem.* **61,** 132–138 (1989).
18. Smith, T. & Stevenson, K. in *Scanning Probe Microscopy* (eds Kalinin, S. & Gruverman, A.) 280–314 (Springer New York, 2007).
19. Amemiya, S., Bard, A. J., Fan, F.-R. F., Mirkin, M. V. & Unwin, P. R. Scanning Electrochemical Microscopy. *Annu. Rev. Anal. Chem.* **1,** 95–131 (2008).
20. Bard, A. & Mirkin, M. *Scanning Electrochemical Microscopy* 2nd ed. (CRC Press, 2012).
21. Ebejer, N. *et al.* Scanning Electrochemical Cell Microscopy: A Versatile Technique for Nanoscale Electrochemistry and Functional Imaging. *Annu. Rev. Anal. Chem.* **6,** 329–351 (2013).
22. Blanchard, P. Y. *et al.* Scanning Electrochemical Microscopy Study of Permeability of a Thiolated Aryl Multilayer and Imaging of Single Nanocubes Anchored to It. *Langmuir* **32,** 2500–2508 (2016).
23. Kai, T., Zoski, C. G. & Bard, A. J. Scanning electrochemical microscopy at the nanometer level. *Chemical Communications* **54,** 1934–1947 (2018).