The electrocatalytic oxidation of ethanol studied on a molecular scale

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CHAPTER 1

INTRODUCTION

This chapter describes the aims of the research in this thesis. Some background information on the concepts of catalysis and electrocatalysis is provided, and a short overview of fuel cell research is presented, in particular related to ethanol electro-oxidation.

1.1 Catalysis

1.1.1 Catalysis and catalysts

Catalysis is one of the most important and widely-spread concepts of chemistry. It has been estimated that 85 - 90% of all chemicals and materials are produced in catalytic processes [1]. In addition, life cannot exist without catalysis, as virtually all biochemical processes that sustain life are reliant on enzymes, nature's own catalysts.

The term catalysis was coined by Berzelius in 1836 [2], and is defined as 'the effect produced in facilitating a chemical reaction, by the presence of a substance, which itself undergoes no permanent change' (as given by the Oxford English Dictionary). Put differently, catalysis is the process of increasing the rate of a chemical reaction by a substance, the catalyst, which is not consumed by the chemical reaction.

The basic principle of catalysis is illustrated by the potential energy diagram in Figure 1.1, which compares the non-catalytic route and the catalytic route of the same reaction. A simplified interpretation of Figure 1.1 is given below. In the non-catalyzed reaction, a high energy barrier has to be overcome for the reactant A and B to form the product P in a single step. This high energy barrier is mainly due to the fact that the reactants must collide in the right configuration for the reaction to occur. As the height of the energy barriers can be directly related to the rate of a reaction, this means a non-catalyzed reaction would be relatively slow. A catalyzed reaction takes place in three general steps. The catalytic reaction starts by bonding the reactants A and B to the catalyst. The catalyst and reactants can be either in the same phase (*e.g.* both in solution), which is termed homogeneous catalysis, or in different phases (*e.g.* reactants in solution and a catalytic surface), termed heterogeneous catalysis. On the catalyst, the reaction takes place to form the product from the reactants. As the catalyst promotes the right configuration of the reactants for the reaction to occur, this barrier is lower than the barrier for the non-catalytic reaction. Finally, the product separates from the catalyst, regenerating the catalyst so it can be used again for the next reaction. In principle, this cycle can be repeated infinitely, although the catalyst can deactivate after a large amount of cycles. Thus, the role of a catalyst is to offer an alternative pathway for the reaction with lower energy barriers, thereby accelerating reactions that would occur at a very slow rate in the absence of the catalyst. Finally, it should be

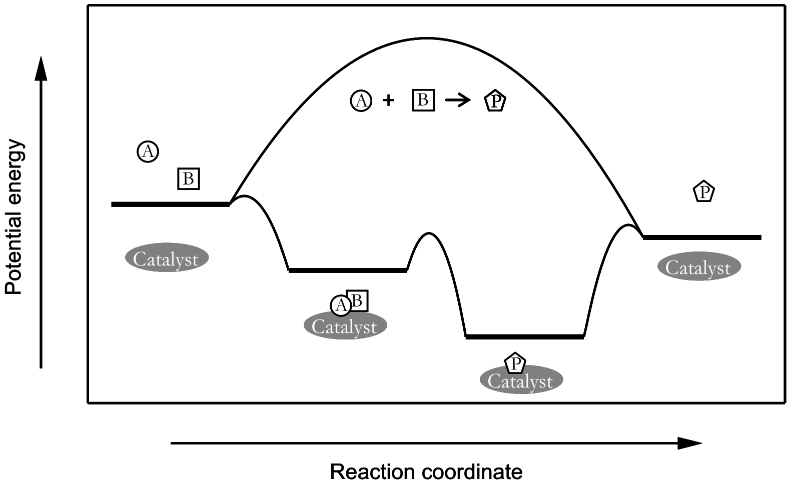


Figure 1.1: *Potential energy diagram of a catalytic reaction. Adapted from Ref 1.*

noted that although a catalysts accelerates a reaction, the final result of the reaction is the same as in the absence of the catalyst.

In a simplified analogue, Figure 1.1 can be compared to a bicycle route through hilly terrain. Suppose there are two routes from the starting point (the left side of the figure; Reactants A and B) to the destination (the right side of the figure; Product P), which are the same length. In the direct route (the uncatalyzed route), the cyclist has to overcome a large hill (a high barrier) to reach the destination. As climbing this large hill requires a large amount of energy, the progress will be slow. Alternatively, the cyclist can take the indirect route (the catalyzed route), which passes over smaller hills. Although this route has more hills (is more complex), the destination will be reached faster as less energy is needed to pass the smaller hills (lower barriers). In addition, although the cyclist uses the indirect route, he does not consume it, but leaves it available for the next cyclist. In other words, after the cyclist has taken the alternative path the path remains intact and can be used by the next cyclist (the catalyst is regenerated and can take part in the next reaction). Although the alternative path can, in principle be used infinitely, the roads may deteriorate after extended use, making it inaccessible at a certain point (deactivation of the catalyst). Finally, it should be emphasized that although the alternative path offers a faster route, the result of reaching destination P is the same is in the direct path (the catalyst changes the reaction pathway but not the final result).

As stated in the introduction, most products and materials are produced through catalytic processes. Since catalysis plays such a large role in society, there is a continuous search for better catalysts, both to optimize existing processes as well as to make promising processes (economically) feasible. Generally, catalysis research aims to improve the following four properties of a catalyst for a given reaction:

- *Activity*. The activity of a catalyst relates to the rate of the catalytic reaction. An ideal catalyst should be able to convert a large amount of reactants into products in a short amount of time.
- *Selectivity*. In most chemical processes, the same (mixture of) reactants can lead to multiple products. An ideal catalyst should accelerate only those reactions that lead to desired products
- *Stability*. Although theoretically a catalyst can be re-used indefinitely, in practice a catalyst can become deactivated over time. An ideal catalyst should be able to partake in the catalytic cycle for a very long time.
- *Cost*. Many catalytic chemical processes are costly. This can, for example, be due to expensive catalyst materials, high energy demands of the process or the need of complex equipment. An ideal catalyst is cheap, both in acquisition and in use.

The research in this thesis will be mainly focused on understanding the parameters that determine the activity, selectivity and stability of the ethanol electro-oxidation reaction (section 1.2.3).

1.1.2 Electrocatalysis

Electrochemistry is the branch of chemistry concerned with the chemical reactions that transfer charge (electrons) across an interface between chemical phases [3], such as the boundary between a solid and a liquid. An electrocatalyst is a catalyst that functions at this interface (boundary). In this thesis, the reaction studied is the conversion of ethanol at the interface of a metal electrode and a

liquid solution. This reaction transfers electrons from the ethanol molecule in solution to the metal electrode, which acts as an electrocatalyst.
At the surface of the electrode under investigation, electrochemical reactions (redox reactions) can occur. These reactions can either provide (oxidation reaction) or withdraw (reduction reaction) electrons from the electrode. Similarly, these electrons can be consumed (of provided) by another electrochemical reaction occurring at another electrode. By connecting the two electrodes in an external circuit, the flow of electrons (the electric current) between the two electrodes can be measured. As these electrons are provided (or withdrawn) by the reaction under investigation, following the electric current is equivalent to following the reaction.

Similar to a general catalyst described in the previous section, an electrocatalyst can accelerate an electrochemical reaction by providing an alternative pathway for the reaction. In the case of an electrode as electrocatalyst, it is possible to directly influence its properties by raising (or dropping) the electric potential of the electrode, thereby increasing (or decreasing) its affinity for electrons and promoting (or inhibiting) reactions at the electrode surface. The difference between the electrode potential at which a reaction actually occurs and the potential at which a reaction should theoretically occur, called the thermodynamical equilibrium potential, is termed the overpotential. For example, the oxidation of ethanol should theoretically occur just above 0.1 V. However, in practice, it only starts at *ca.* 0.4 V on a platinum electrode. Thus, the oxidation of ethanol on platinum has an overpotential of *ca.* 0.3V. A large part of electrocatalysis deals with finding the electrocatalyst that minimizes the overpotential for the desired reaction.

1.1.3 Model catalysts

In practical applications, most (electro-)catalysts are complex systems. In addition, most reactions are performed at elevated temperatures and/or elevated pressures. For example, the ideal operating temperature of the well-known automotive exhaust catalyst lies between 350 and 650 °C, and an electrocatalytic hydrogen fuel cell operates around 80 °C. Furthermore, in both these cases, the catalyst consists of small (nanometer range) noble metal particles, anchored to an inert support material to minimize the amount of catalyst needed. In addition, these metal particles are not uniform: the size, shape and composition of one

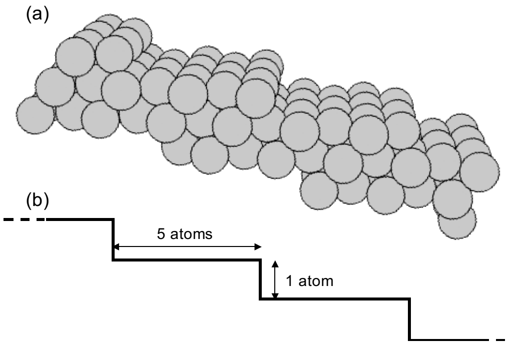


Figure 1.2: *Representations of a platinum (553) single-crystal surface: (a) atom model and (b) schematic representation.*

particle might differ strongly from the next. Clearly, it is difficult to study the fundamental aspects of a certain catalytic reaction in such a complex system.

Therefore, in fundamental studies the complex catalytic system is often replaced by a simplified model. In the research presented in this thesis a ‘surface science’ approach has been adopted, replacing the poorly defined ensemble of supported metal particles as a catalyst by a metal surface which is better defined and therefore less complex, such as a single-crystal surface, which is well-defined on an atomic level. An example of a single-crystal surface, Pt (553), is shown in Figure 1.2. It can be seen that the surface has a certain periodicity in the form of a staircase-like structure. This surface consists of flat terraces (the treads of the staircase) of five atoms wide, separated by steps (the risers of the staircase) of one atom high. By varying the width of the terrace (or, similarly, the amount of steps) in a controlled manner, it is possible to obtain a range of surfaces with a systematic change in the surface structure. In a fundamental catalysis study, analyzing the catalytic performance of a range of single-crystal surfaces can yield important insights into how the surface structure affects the catalytic process. Furthermore, the use of model catalysts allows the use of multiple characterization techniques not available for ‘real’ catalysts.

1.2 Fuel cell systems

1.2.1 Historical overview

The history of fuel cells is an intriguing subject in the history of electrical energy conversion systems [4]. The invention of the fuel cell is often attributed to Sir William Grove, who, in 1839, reported that a current could be generated by passing hydrogen and oxygen gas over platinum electrodes in a dilute sulfuric acid solution [5]. The development of fuel cells, however, lacked a drive for the next century, as fossil fuels were abundant, and as a result the internal combustion engine became the primary power source. Only after the Second World War, a renewed interest in fuel cell technologies appeared due to the emerging space flight programs, which demanded a light, reliable, non-combustion based power source.

One of the first fuel cells developed was the alkaline fuel cell in the 1950s, which was used in the Apollo missions. The alkaline fuel cell employed nickel-based electrodes in a circulating potassium hydroxide solution. Although this fuel cell offers one of the highest electrical efficiencies, it is restricted to very pure hydrogen and oxygen gas, barring the wide-spread adoption in general applications.

Since the 1970s, the emergence of another social concern furthered the ongoing investigation into fuel cells as energy sources. Due to the oil crises in 1973, it had become clear that the availability of fossil fuels is not limitless and alternative, renewable energy sources and technologies are desired.

Due to the inherent requirement for very pure gasses in alkaline fuel cells, and the development and commercialization of stable, conducting membrane materials, such as Nafion, research interests shifted to the development of polymer electrolyte membrane (PEM) fuel cells. In these PEM fuel cells, the electrodes are separated by a conducting membrane. Oxygen (from air) is supplied to one electrode, while the fuel is fed to the second electrode. Initially, the fuel was envisioned to be hydrogen, similar to the alkaline fuel cells. Problems with production, transportation and storage of hydrogen [6] have, however, led to consider small alcohols (such as methanol or ethanol) as potential fuels in a direct alcohol fuel cell (DAFC). Since these fuels are liquid, most practical issues associated with the use of hydrogen gas can be circumvented. In addition, methanol and ethanol can be obtained from sustainable resources and offer a high theoretical power to weight ratio.

So far, this section has focused on low temperature fuel cell technologies (operating temperatures 60 - 100 °C), which are envisioned for mobile applications. Apart from these low temperature fuel cells, there is a branch of research into high temperature fuel cells, such as the molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). Due to the high technical demands related to high operating temperatures (600 - 1000 °C), these fuel cells are more suited for stationary application, such as (small) power plants.

1.2.2 Basic working principle of a fuel cell

A fuel cell is a galvanic cell, which converts the energy released in a chemical reaction into electrical energy through an electrical current. In this section, the basic working principle of a fuel cell will be discussed briefly.

A schematic drawing of a basic hydrogen/oxygen fuel cell is shown in Figure 1.3. The basic structure can be generalized to all fuel cells: the cell consists of two electrodes, which are separated by an electrolyte, a medium which provides the electric conductance in the fuel cell, and are connected in an external circuit. The fuel (hydrogen (H_2) in Figure 1.3) and the oxidant (oxygen (O_2) in Figure 1.3) are supplied to the two electrodes (the fuel to the anode and the oxidant to the cathode), at each of which a half-reaction occurs.

In the case of a hydrogen/oxygen fuel cell, the following half-reactions take place:

Anode: $2\ H_2 \rightarrow 4\ H^+ + 4e^-$ $E^0 = 0.00$ V.
Cathode: $O_2 + 4\ H^+ + 4e^- \rightarrow 2\ H_2O$ $E^0 = 1.23$ V.

Adding these half-reaction give the following overall reaction:

$$2\ H_2 + O_2 \rightarrow 2\ H_2O \qquad \Delta E^0 = 1.23\ \text{V.}$$

At the anode, the electrode at which the electrons are provided by the chemical reaction, hydrogen gas is converted to protons (H^+) and electrons (e^-) in an oxidation reaction. The protons enter the electrolyte and are transported to the cathode, the electrode at which the electrons are consumed by the chemical reaction. The electrons flow through the external circuit toward the cathode, providing an electrical current. Oxygen gas is supplied to the cathode. Here, the oxygen molecule recombines with the protons coming from the electrolyte and

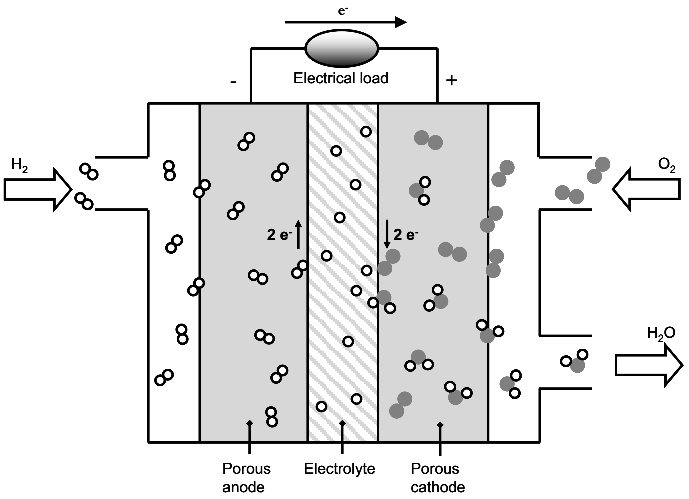


Figure 1.3: *Schematic drawing of a hydrogen/oxygen fuel cell. Adapted from Ref 4.*

electrons coming from the external circuit to form two molecules of water in a reduction reaction. Therefore, the overall reaction is the formation of water (H_2O) from hydrogen and oxygen, with the water being formed at the cathode. The theoretical potential provided by a hydrogen/oxygen fuel cell under standard conditions is 1.23 V, the difference in the equilibrium potentials of the half-reactions.

1.2.3 Direct ethanol fuel cell

As discussed before, using ethanol at the anode of a fuel cell rather than hydrogen has a number of distinct advantages. First, ethanol is a liquid at room temperature and can be easily introduced in the current fuel distribution and storage systems. Furthermore, ethanol can easily be produced in large quantities. Ideally, ethanol could be produced by the fermentation of biomass, such as agricultural waste, capturing carbon dioxide (CO_2), a greenhouse gas, in the process. Since the oxidation of ethanol would release the captured carbon dioxide, the entire cycle would be carbon neutral. In other words, there would be no overall CO_2 emission or capture. In addition, both ethanol and its (final) oxidation product carbon dioxide have a very minimal toxicity.

In the case of a direct ethanol fuel cell (DEFC), ethanol (CH_3CH_2OH) is supplied to the anode as a fuel rather than hydrogen. Ideally, this would lead to the following reactions:

Anode: $CH_3CH_2OH + 3\ H_2O \rightarrow 2\ CO_2 + 12\ H^+ + 12\ e^-$ $E^0 = 0.10$ V.
Cathode: $3\ O_2 + 12\ H^+ + 12\ e^- \rightarrow 6\ H_2O$ $E^0 = 1.23$V.

Overall: $CH_3CH_2OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$ $\Delta E^0 = 1.13$V.

Comparing these reactions with the reactions of a hydrogen fuel cell shows that, in a DEFC the protons and electrons needed to convert oxygen to water are supplied by the ethanol molecule rather than hydrogen gas. Using ethanol also leads to an extra emitted product, carbon dioxide. The theoretical potential of a direct ethanol fuel cell is 1.13 V, close to that of hydrogen/oxygen fuel cell. However, the issues in the development of direct ethanol fuel cells are considerable:

- The oxidation of ethanol does not only produce carbon dioxide, but also yields undesired products which have a significant lower energy output and are unwanted due to their harmful nature, such acetaldehyde and acetic acid [7, 8].
- The oxidation of ethanol to carbon dioxide proceeds through intermediates which adsorb (bond) strongly to the electrode surface, inhibiting the catalytic activity of the electrode [8].
- Low activities require a large amount of catalyst, which generally consists of noble metal, in order to produce a sufficiently high power output, making DEFCs costly.
- The oxidation of ethanol is sluggish near the equilibrium potential. Therefore, the oxidation of ethanol requires a high overpotential, decreasing the efficiency of a fuel cell [9].
- Dissolved ethanol can cross-over to the cathode, leading to a considerable decrease in the efficiency [10].
- An alkaline electrolyte would increase the rate of the oxidation of ethanol (anode) and of the reduction of oxygen (cathode), leading to higher energy output. However, the ethanol oxidation product carbon dioxide is quickly converted to carbonate in an alkaline electrolyte, decreasing the efficiency [11].

In the following sections, results published previously in literature on the oxidation of ethanol will be discussed.

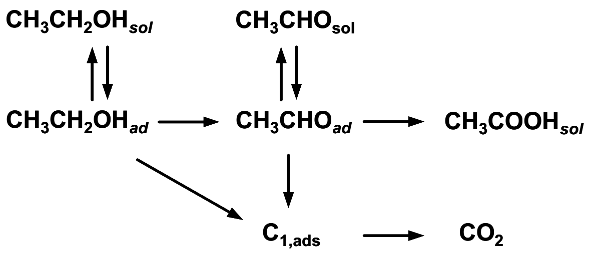
1.3 Electrocatalytic oxidation of ethanol

1.3.1 Ethanol oxidation on platinum

The electrochemical oxidation of ethanol on platinum has been studied extensively [9, 12-21]. Already in early studies it was found that that the main products of ethanol oxidation are acetaldehyde [17, 18] and acetic acid [19] rather than CO_2. Apart from the loss of efficiency, acetic acid is also unwanted as it constitutes a catalyst poison. The complete oxidation product carbon dioxide is only found to a minor extent [20, 21]. It is generally assumed that that the various reaction products are formed by the pathways shown in Scheme 1.1.

The oxidation of ethanol is initiated by the adsorption of ethanol (CH_3CH_2OH) on a vacant surface site. After adsorption, ethanol can be converted to (weakly adsorbed) acetaldehyde (CH_3CHO). Acetaldehyde can desorb and diffuse into the bulk of the solution, or remain adsorbed (or re-adsorb) to be converted to acetic acid (CH_3COOH). Alternatively, the carbon-carbon bond can be broken in adsorbed ethanol and/or adsorbed acetaldehyde, forming strongly adsorbed single carbon species. Finally, the adsorbed C_1-fragments can react with adsorbed OH species (originating from water) and be oxidized to CO_2.

The first molecular-level study of products and intermediates of ethanol electro-oxidation was provided by Willsau and Heitbaum [17] with the use of differential electrochemical mass spectrometry (DEMS). They identified CO_2 and acetaldehyde as the primary reaction products, although it should be noted that acetic acid is not volatile enough to be detected by DEMS. By employing deuterium and ^{18}O labeling, this study showed that acetaldehyde is formed by the cleavage of hydrogen atoms from the hydroxyl group and the α-carbon of ethanol. Furthermore, it was found that CO_2 is formed through a strongly bound intermediate, which is oxidized to give two CO_2 molecules, one originating from the methyl group and the other from the alcohol group and still containing the alcoholic O. Subsequent DEMS measurements [15, 22] studied the C-C bond breaking in more detail. By isotopic labeling of the carbons in ethanol, methane



***Scheme 1.1**: Schematic representation of the various ethanol oxidation pathways*

and ethane originating from the methyl group of ethanol was detected during slow cathodic potential sweeps into the hydrogen adsorption region after ethanol adsorption at potentials before the onset of CO_2 evolution, indicating C-C bond breaking and CO_2 production to be decoupled processes.

Most studies on ethanol oxidation on platinum single crystal electrodes have focused on the structure sensitivity of the formation of the different products, mainly on the basal planes of platinum. By studying the early stages of adsorption and oxidation of ethanol on platinum with *in situ* Fourier transform infrared spectroscopy, Xia *et al.* [21] found that the onset potential for ethanol dissociation, as followed by the CO_{ad} infrared absorption intensities, coincides with the hydrogen desorption potential. In addition, the presence of adsorbed CO strongly inhibited further oxidation on all surfaces. By relating the spectroscopic measurements with the voltammetric data, it was concluded that the surface sites covered with CO_{ad} and thus the capacity to cleave the C-C bond is higher on Pt (100) than on Pt (111) or Pt (110). It is also worth noting that the amount of CO_2 produced keeps increasing after the surface becomes free of CO_{ad}, indicating the presence of other strongly adsorbed species, likely CH_x, which is not observable by infrared spectroscopy.

Infrared spectroscopy has also been employed to follow the formation of acetaldehyde and acetic acid platinum during ethanol electro-oxidation. On the basal planes, acetaldehyde could be observed starting at about 0.4 V vs. RHE, well before the onset of CO oxidation, while the onset of acetic acid formation closely follows CO_2 formation [20, 21]. This is readily explained by the fact that both CO oxidation and acetic acid formation require a common adsorbed co-reactant, OH_{ad}, whereas the formation of acetaldehyde from ethanol merely involves a relatively simple proton-electron transfer.

So far, few studies have focused on the effect of (the concentration of) defect sites, as modeled by using platinum single crystal electrodes with varying step density. A notable exception is a study by Tarnowski and Korzeniewski [23], who followed the quantities of acetate formed at different potentials in potential step experiments using ion chromatography on Pt (111), Pt (755) ≡ Pt [6(111)x(100)] and Pt (533) ≡ Pt [4(111)x(100)]. It was shown that, although the maximum currents increased with step density, the relative contribution of acetic acid formation decreased. Since step sites are assumed to facilitate C-C bond breaking in ethanol oxidation [24], this decreased activity was partly attributed to increased surface poising blocking sites for water adsorption, thereby inhibiting acetic acid formation. Since the maximum currents do increase with step density, it is likely that other processes, such as acetaldehyde formation, become more pronounced on (partially blocked) stepped surfaces [25].

Since several steps in the ethanol oxidation mechanism require the presence of an OH_{ad} species, the use of an alkaline medium has also attracted some attention due to the ubiquitous hydroxide ions, leading to significantly higher oxidation currents. However, for fuel cell purposes, one has to consider the progressive carbonation of the electrolyte solution due to CO_2, which is produced as a product of the oxidation reaction, leading to a decrease of the pH of the solution. A study on the electro-oxidation of C_1-C_4 alcohols by Tripković *et al.* [26] on Pt (111), Pt (755) ≡ Pt [6(111)x(100)] and Pt (332) ≡ Pt [5(111)x(110)] in an alkaline electrolyte has shown that the potentials at which ethanol can be oxidized are mainly effected by the ability of the surface to adsorb OH^- anions. On all three surfaces, the onset potential of ethanol oxidation coincides with the completion of hydrogen desorption and accelerates in the potential region in which the hydroxide anions can adsorb reversibly. The peak potential in all cases was found to be coupled to the onset of the irreversible hydroxide adsorption or oxide layer formation, which occurs at a lower potential on the stepped surfaces than on Pt (111).

1.3.2 Ethanol oxidation of other metals

As platinum itself is not active enough to be commercially interesting for a DEFC, research attention has also been focused on finding more active materials. At the same time, considerable effort has been undertaken to increase the selectivity towards CO_2.

One of the metals that has attracted interest for use as an electrode material in the ethanol oxidation reaction is rhodium, at least from a fundamental point of view. It is found that rhodium is a far less active catalyst for the ethanol electrooxidation reaction than platinum [25, 27]. Similar to ethanol oxidation on platinum, the main reaction products were CO_2, acetaldehyde and acetic acid. Rhodium, however, presents a significant better CO_2 yield relative to the C_2-compounds than platinum, indicating a relatively higher C-C bond breaking activity. This increased ability to activate the ethanol carbon-carbon bond is also reflected in cathodic scans, during which the sole reduction product was methane.

The lower total activity for rhodium electrodes may be partly due to increased CO poisoning compared to platinum electrodes, as demonstrated by the number of voltammetric cycles required to oxidize a saturated CO adlayer from rhodium electrodes [28]. In addition, it is argued that the barrier to dehydrogenation is higher on rhodium than on platinum, leading to a lower overall reaction rate [27]. These effects may also explain the lower product selectivity towards acetaldehyde and acetic acid, which require the dehydrogenation of weakly adsorbed species.

Palladium has also been investigated widely, especially in alkaline media, due to the fact that it has already shown a high activity for the methanol oxidation reaction [29]. Recently, it was shown that the activity towards the ethanol oxidation reaction in alkaline media is slightly higher on palladium than on platinum [30]. In addition, palladium was found to display a better steady state behavior than platinum [30]. Mechanistic studies of the ethanol oxidation reaction on palladium show that adsorption of ethanol on the electrodes surface is facile [31]. However, the ethanol oxidation reaction on palladium suffers from the same selectivity problem as on platinum: the main reaction products are acetaldehyde and acetate, while carbon dioxide production occurs only to a small extent [31-34].

Another metal that has received some attention is gold. As gold does not break the carbon-carbon bond in ethanol, it can be used as a model catalyst to study the pathway leading to acetaldehyde and acetic acid. Gold is generally considered a poor electro-catalyst for oxidation of small alcohols, particularly in acid medium. In alkaline medium however, the reactivity increases, which is related to that fact that no poisoning CO-like species can be formed or adsorbed on the surface [35, 36]. Similar to platinum electrodes, the oxidation of ethanol starts at potentials corresponding to the onset of surface oxidation, emphasizing the key role of surface oxides and hydroxides in the oxidation process. The only product observed upon the electro-oxidation of alcohol on gold in an alkaline electrolyte is acetate, the deprotonated form of acetic acid. The lack of carbon dioxide as a reaction product again suggests that adsorbed CO-like species are an essential intermediate in CO_2 formation.

In an acidic medium, the reactivity of ethanol on gold electrodes is much lower than in alkaline media. The main product of the oxidation of ethanol on gold in an acidic electrolyte was found to be acetaldehyde, with small amounts of acetic acid [36]. The different reactivities and the product distributions in different media were explained by considering the interactions between the active sites on gold, ethanol and active oxygen species absorbed on or near the electrode surface. In acidic media, surface hydroxide concentrations are low, leading to the relative slow dehydrogenation of ethanol to form acetaldehyde to be the main oxidation pathway. In contrast, in alkaline media, ethanol, adsorbed as an ethoxy species, reacts with a surface hydroxide forming adsorbed acetate, leading to acetate (acetic acid) as the main reaction product.

1.3.3 Ethanol oxidation on bi- and trimetallic electrodes

An alternative approach that has been taken to find more active materials has been to modify platinum with a second or even third metal [9]. The added metal can generally enhance the activity through two mechanisms: a bifunctional mechanism [37] in which the second component provides one of the reactants, and a ligand or electronic effect [38] where the second component alters the electronic properties of the original metal.

Inspired by the positive effect on the electro-oxidation of methanol [39-41], one of the systems that has been studied extensively is the platinum-ruthenium bimetallic system. The most dominant mechanism for the promoting effect of ruthenium was for a long time thought to be the bifunctional mechanism: the more oxophilic ruthenium acts as an oxygen donor (usually believed to be adsorbed hydroxyl, by oxidizing water at a lower overpotential), which reacts with CO adsorbed on platinum to give CO_2. However, weakening of the CO-bond to platinum in the presence of ruthenium has also been observed in UHV experiments[42] and DFT calculations[43, 44], indicating a significant electronic effect. In light of this, ruthenium could also be expected to enhance ethanol oxidation on platinum. Schmidt *et al.*[45] and Fujiwara *et al.*[46] have reported that the addition of ruthenium shifted the onset potential for product species negatively (*i.e.* lower potential), although a loss in overall activity was observed. In order to mechanistically study the effect of ruthenium, the ratio between platinum and ruthenium at the surface has to be determined precisely, which can significantly alter the activity and the product selectivity of the ethanol oxidation reaction [46]: in the range of 0-50 atomic % of ruthenium on the surface, the highest selectivity towards carbon dioxide was found for a high ruthenium content. For a ruthenium content of 50% no acetaldehyde formation was observed, the only detected reaction product was carbon dioxide (the DEMS technique employed in the study could not detect the non-volatile acetate) [46]. The total catalytic activity was first found to increase, then decrease with increasing ruthenium content: addition of small amounts of ruthenium increase the amount of adsorbed hydroxyl species available for oxidation, but higher amounts of ruthenium causes the reaction to be limited by the smaller probability of ethanol adsorption on the platinum sites of an electrode.

Platinum-tin bimetallic compounds have been studied as a catalyst for ethanol electro-oxidation by means of infrared spectroscopy [47, 48], XRD [49] and TEM [49]. Platinum-tin bimetallic systems were found to show higher overall oxidation activity, but little effect was found on the overpotential needed for ethanol oxidation. It has been suggested that the main effect of tin addition is to improve the bifunctional mechanism [49]. Furthermore, calculations [50] and experimental results [51] indicate that CO does not adsorb on tin, while it can adsorb on some sites of ruthenium, explaining the enhanced activity of tin over ruthenium in ethanol electro-oxidation, due to less surface poisoning. However, this means that the enhanced activity of platinum-tin catalyst is mainly related to improving acetaldehyde/acetic acid production, while having little effect on the carbon dioxide formation.

Another commonly studied bimetallic system is the platinum-rhodium system, which is widely employed in the exhaust systems of automobiles for NO_x reduction and CO oxidation. Furthermore, platinum-rhodium electrodes have been known to be CO-tolerant catalysts for molecular H_2 oxidation [52]. Analyzing DEMS and *in situ* FTIR results, De Souza *et al.* [27] have observed a direct correlation between the platinum/rhodium ratio and the activity and selectivity of the catalysts: an increasing rhodium content has a significant positive effect on the selectivity towards total oxidation to CO_2. On the other hand, the best total oxidation activity was found for pure platinum and decreases with increasing rhodium content. The decreasing reaction rate can probably be ascribed to the lower dehydrogenation activity of rhodium and apparently strong CO-rhodium interaction as revealed by the difficulty of totally removing a CO monolayer from a rhodium electrode [28].

Since no single metal addition to platinum gives the desired effect of improving the total catalytic activity as well as the product selectivity to carbon dioxide, it is crucial to develop catalysts that improve both catalytic aspects. A common approach is to modify a platinum-ruthenium or a platinum-tin system with a third metal that improves the carbon-carbon bond breaking rate. A system has received notable attention is the trimetallic platinum-rhodium-tin system [53-56]. This system shows promising results regarding both activity and selectivity of the ethanol oxidation reaction. However, it should be kept in mind that platinum-rhodium-tin electrocatalysts have been investigated only recently and require ongoing research activities before they can be implemented in DEFCs. Finally, the question remains whether the supplies of noble metals as platinum and rhodium are sufficient for such electrocatalysts to become economically viable.

1.4 Scope of this thesis

The research presented in this thesis is focused on elucidating the mechanism and the kinetics of the electro-oxidation of ethanol, leading to the reaction products acetaldehyde, acetic acid and carbon dioxide.
In Chapter 2, the experimental set-up will be discussed. In addition, an overview of the different electrochemical and spectroscopic techniques employed in this thesis will be given.

In Chapter 3, the electro-oxidation of ethanol in acidic media on a series of Pt [*n*(111)x(111)] single-crystal electrodes is investigated. Voltammetric and chronoamperometric data illustrate how the surface structure influences the various steps in the ethanol electro-oxidation mechanism.

Chapter 4 deals with the issue of product selectivity regarding the results presented in Chapter 3. By following the reaction products with online electrochemical mass spectrometry (OLEMS), it was found that the influence of the surface structure on the product distribution is strongly dependent on the nature of the electrolyte.

In Chapter 5, the (electro-)chemical nature of strongly adsorbed intermediates during the electro-oxidation of ethanol in acidic media was investigated using surface enhanced Raman spectroscopy (SERS). By comparing the intermediates with the intermediates from deuterated ethanol, CH_{ad} was observed as an essential intermediate towards the full oxidation of ethanol.

Chapter 6 reports a study of the ethanol electro-oxidation reaction in alkaline media, employing single-crystal electrodes to elucidate the role of the electrode surface structure and SERS to identify the strongly adsorbed intermediates. A key difference with the oxidation in acidic media was found in the reactivity of $CH_{(x)ad}$ species.

In the last chapter, Chapter 7, the effects of electrolyte pH and composition was studied with multiple techniques on polycrystalline electrodes. A pronounced enhancement in the activity was found for pH > 10 on both platinum and gold electrodes.

1.5 References

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