Electrooxidation of Small Organic Molecules at Elevated Temperature and Pressure: An online Differential Electrochemical Mass Spectrometry (DEMS) Study

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Chapter 1

Introduction
1.1 Which is the winner: energy supply or energy demand?

Nowadays, an enormously increasing demand for energy (from 14 terawatts in the year 2000 to 28 terawatts by the year 2050 [1,2] together with the increase in global population represents a great challenge for the energy supply, which is crucial and necessary to maintain / secure improvement of human living conditions. However, most of the energy sources are constituted from fossil fuel (major forms are petroleum, coal and natural gas), which are non-renewable (need millions of years to form) and diminishing (“energy crisis” in a worst case) with growing demands. On the other hand, fossil fuels as an energy source are initiating environmental problems, such as climate changes, global warming, melting of ice caps, acid rains, air pollution and so on. It is reported [3] that the fossil fuel consumption distribution in the overall energy sources in the year of 2010 is as follows: petroleum is 33.6%, coal is 29.6% and natural gas is 23.8%. Furthermore, more and more concerns are placed on environmental, climatic and sustainable issues related to renewable and clean energy sources, such as wind power, hydroelectric power, solar energy, biomass and bio-fuel, geothermal energy, ocean tide and wave power and so on, which are potential candidates for satisfying the increasing energy demands and challenges. Especially, thanks to the rapid development in nanotechnology and catalysis science, this offers a requisite option in generating renewable and environmentally friendly energy in large scale. The further requirement will focus on improving the utilization efficiency during the energy conversion process comparing to the inefficient direct combustion of fossil fuels.

1.2 Fuel cells – high-efficiency energy alternative

1.2.1 Classification of fuel cells

Fuel cell (FC), a kind of electrochemical device, which can directly (avoiding combustion cycles as present in internal combustion engines) and continuously (as long as fuel and oxidant are supplied) convert the free energy in a chemical reaction into electrical energy as well as heat, provides a new option in power generation with an advantage of high conversion efficiency to meet the needs mentioned above.
As far as electrochemical technologies behind the electrochemical devices are concerned, they include electrochemical energy conversion (fuel cells), electrochemical energy storage (batteries and electrochemical capacitors) and electrochemical synthesis [4,5]. Essentially, a fuel cell (belongs to one kind of galvanic cell) is similar to a conventional battery, with the main difference in the way of transforming the chemical energy into electrical energy:

- a battery utilizes the chemical energy “stored” within the reactant, which can be under operation until the reactant are completely depleted, resulting in two possibilities: either re-charged (secondary battery) or just thrown away (primary battery),
- a fuel cell “converts” the chemical energy into electrical energy through external reactant supply providing electrical output as long as the supply of fuel is maintained.

Fuel cells can be mainly classified into following types of technologies [6-8] according to the electrolyte employed and summarized as follows [9-11] (shown in Figure 1.1):

![Figure 1.1 General schematic representations of working principles for types of fuel cells. The respective fuel is electrooxidized on the anode producing protons / conducting ion and electrons. The electrons flow around an external circuit powering a load whereas the protons / conducting ions (OH\(^-\) for AFCs, \(\text{CO}_3^{2-}\) for MCFCs, and \(\text{O}_2^3\) for SOFCs) migrate though a conductive electrolyte, which separates the anode and cathode. On the cathode, oxygen molecules combine with the protons and electrons and are then further electroreduced into water. Figure adapted from [10].]
Alkaline fuel cells (AFC), Proton exchange membrane fuel cells (PEMFC), Direct small organic molecules oxidation fuel cells, such as direct methanol fuel cells (DMFC), direct ethanol fuel cells (DEFC), phosphoric acid fuel cells (PAFC), Molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC).

In addition, according to the operating temperatures, the latter two types of fuel cells (MCFC and SOFC) can be further classified as high temperature fuel cells (above 650°C) for large-scale application in stationary power generation (in MW scale), while AFC, DMFC / DEFC and PEMFC can be sorted into low temperature fuel cells (below 120°C) aiming at mobile / portable electronic (1-100 W) and transportation (20-200 kW) applications.

1.2.2 Low temperature PEMFC: fundamental concepts

As mentioned above, the challenges for renewable and environmentally friendly (reducing pollutions and greenhouse gases) energy sources as an alternative to fossil hydrocarbons for securing the energy supply for the whole society, research and development (R&D) on high-efficiency fuel cell technology definitely requires a broad range of understanding in scientific interdisciplinary knowledge, such as chemistry, electrochemistry, (electro)catalysis, material science, thermodynamic, kinetic, electrical engineering and so on.

Hydrogen, the most abundant element in the nature and a kind of clean energy carrier (rather than energy source), has attracted more interest since 1839 when Sir William Grove demonstrated a H₂/O₂ fuel cell in acidic electrolyte.

For the H₂/O₂ PEM fuel cells, the corresponding reactions are as follows,

Anode: \[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad \text{E}^\circ (\text{H}_2/\text{H}_2\text{O}) = 0 \text{ V} \]

Cathode: \[ \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \quad \text{E}^\circ (\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V} \]

Overall reaction: \[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \text{E}^\circ (\text{cell}) = 1.23 \text{ V} \]

The resulting standard reversible cell potential is 1.23 V, which is acquired at standard conditions (i.e., pH = 0, \( T = 298 \text{ K}, P_{\text{reactant}} = 1 \text{ bar} \)). It results from basic thermodynamic principles: \( \Delta G^\circ = -nF\text{E}^\circ \), where \( \text{E}^\circ \) is called the standard emf (electro motive force) of the cell reaction [12]. Furthermore, according to the basic thermodynamic equation: \( \Delta R \text{G}^{(T)} = \)
where the Gibbs free energy \( \Delta R G(T) \) (for \( \Delta T = 0 \)) describes the part of chemical energy of the fuel that can theoretically be converted into electrical work and \( T \cdot \Delta R S(T) \) represents the enthalpy that can only be converted into heat, which is an irreversible loss in the energy conversion. Thus, the maximum electrical efficiency (\( \eta_{el} \)) is given by relationship: 

\[
\eta_{el} = \frac{\Delta R G(T)}{\Delta R H(T)}.
\]

Taking a H\(_2\)/O\(_2\) fuel cell for example, \( \Delta G(25^\circ C) = -237.3 \text{ kJ mol}^{-1} \) and \( \Delta H(25^\circ C) = -286.0 \text{ kJ mol}^{-1} \), resulting in a maximum (theoretical) electrical efficiency (\( \eta_{el} \)) of 83% at 25°C.

The anodic hydrogen reactions (\( \text{H}^+ + e^- \leftrightarrow \frac{1}{2} \text{H}_2 \)) in the general reversible case, include the hydrogen evolution reaction (HER) with proton discharging to form molecular hydrogen and the hydrogen oxidation reaction (HOR) with discharging of adsorbed hydrogen atoms into protons and electrons. Until now, much effort has been devoted to understand the kinetics and mechanism of these reactions, aiming at widespread application in fuel cells with low-cost and more efficient electrocatalysts [13]. The catalysts for the electrocatalytical hydrogen reactions are selected and optimized based on the comprehensive understanding from theoretical studies of computational methods, such as density functional theory (DFT) or Monte Carlo simulations, in combination with the knowledge from surface science and catalysis. The interpretation of hydrogen adsorption, based on the corresponding theory (“d-band model”) developed by Hammer and Nørskov [14,15], can be described as its interaction with the d-orbitals of the metal. The activity for hydrogen oxidation / evolution can be generally described by plotting the exchange current density against the hydrogen metal bond strength. This produces a volcano plot [16,17], in which platinum shows the best activity for the HER. Actually, the characteristic of this volcano plot is related to the Sabatier principle [18], which requires that the binding energy between surface and adsorbates be moderate – neither too strong nor too weak. The former case will cause poisoning of the catalyst surface, and the latter case will result in decreasing adsorption on the catalyst surface, so that reaction can not take place.

In a microscopic picture, hydrogen reactions can be described by the follows processes: i) dissociative adsorption, chemisorption and charge transfer process in the electrode-electrolyte interface attaining to a significant coverage of chemisorbed H atom on some noble-metal (such as Pt, Pd and Rh) electrodes surface. Traditionally, the HOR / HER can be further
described by a predictive model based on classical concept using Butler-Volmer equation to describe the characteristic relationship between the catalyst-dependent exchange current density and the electrode potential referenced to the equilibrium potential [12].

However, the Butler-Volmer equation does not represent the elementary reaction step, where the overall reaction depends on the slowest elementary reaction (rate determining step). Generally, the elementary reaction steps in acid solution can be described as follows [13,19-21]

\[
\begin{align*}
H_{\text{ads}} & \rightleftharpoons H^+ + e^- \quad \text{(Volmer reaction)} \\
H_2 & \rightleftharpoons H_{\text{ads}} + H_{\text{ads}} \quad \text{(Tafel reaction)} \\
H_2 & \rightleftharpoons H^+ + H_{\text{ads}} + e^- \quad \text{(Heyrovski reaction)}
\end{align*}
\]

The corresponding mechanism can be interpreted by the combination with two of the above mentioned pathways during hydrogen reaction:

1. The combination of Volmer and Tafel reaction results in the “Volmer-Tafel mechanism”, with a proton discharged and adsorbed hydrogen atom formed on the electrocatalyst surface, followed by the formation of hydrogen by combination of two adjacent adsorbed hydrogen atoms.

2. The “Volmer-Heyrovski mechanism” with a proton discharged on the electrocatalyst surface resulting in the formation of an adsorbed hydrogen atom, followed by the formation of H$_2$ by reaction with another proton and an electron.

It was proposed by Quaino et al. [22] based on HOR experiments on a Pt microelectrode that the Volmer-Tafel pathway dominates the HOR at low overpotential, while at higher overpotential, the Volmer-Heyrovski mechanism prevails.

The cathodic oxygen reduction reaction (ORR), which alleviated not only fundamental interest, but has a clear perspective also for technical applications [23], is more complex than the hydrogen reactions (HER / HOR). It involves transfer of 2-4 electrons in a number of elementary steps (oxygen adsorption, charge transfer, breaking of the O-O bond, desorption and so on), resulting in different reaction intermediates. The complicated reaction scheme can be described in the following way [19,24-28]:
(1) **Direct 4-electron reduction pathway or parallel pathway:** O$_2$ molecules are directly electrochemical reduced to H$_2$O (O$_2$ + 4H$^+$ + 4e$^-$ $\rightarrow$ 2H$_2$O, E° = 1.23 V$_{RHE}$).

(2) **Indirect pathway or “series” 2-electron reduction:** O$_2$ molecules are first reduced to H$_2$O$_2$$_{,ad}$ (O$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$O$_2$, E° = 0.67 V$_{RHE}$), which can be further reduced to H$_2$O (H$_2$O$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ 2H$_2$O, E° =1.77 V$_{RHE}$), or desorbs into the bulk solution, or catalytically decomposes into H$_2$O and O$_2$ (2H$_2$O$_2$ $\rightarrow$ 2H$_2$O + O$_2$). In the latter case the dissociation energy of the H$_2$O$_2$ molecule is 146 kJ mol$^{-1}$, which helps facile reduction on the electrode surfaces.

Furthermore, theoretical studies [28] based on density functional theory (DFT) predicts a volcano-shape relationship between the rate of the cathode reaction (ORR) and the O and OH binding energies. These authors by a proposed that the ORR can proceed via

(i) **a dissociation mechanism:** dissociation of O$_2$ to generate two oxygen atoms on the surface as the first reaction step, followed by the reaction with H$_{ad}$ to form water at potentials and oxygen coverage where O$_2$ dissociation is activated,

(ii) **an associative mechanism:** direct proton / electron transfer to O$_{2,ad}$ to produce OOH formation without O$_2$ dissociation [28-30].

H$_2$O$_2$ formation is experimentally detected and quantified using the second electrode (collector) in a rotating (ring) disk electrode [31-36] or in a double disk dual thin layer flow cell [37,38] configuration. The role of the peroxide played in the oxygen reduction reaction is assumed to be either an intermediate and / or a spectator species [19]. In a practical fuel cell, the 4-electron direct reduction pathway is desirable for obtaining maximum efficiency and avoiding possible corrosion of carbon supports or membrane by peroxide. Thus, studies on the influence of variable reaction parameters on the selectivity of the ORR attracted significant interest. For instance, the loading effect [39-43] on the selectivity (peroxide formation) could be reasonably explained by the fact that increasing the catalyst loading results in a thicker catalyst layer, which increases the probability for further reduction of peroxide to water [44]. Moreover, if the oxygen molecule is reduced to hydrogen peroxide, can be further reduced to water on the metal (Pt) surface [45], the probability of re-adsorption and further reaction increases with increasing catalyst (Pt) loading [45].
It has to be mentioned that the equilibrium voltage derived from thermodynamics in both hydrogen reactions (HOR / HER) and oxygen reduction reaction (ORR) can not be measured in practice due to the overpotential (or overvoltage). The relation between the measured current and the deviation of the electrode potential from the equilibrium potential, the overpotential $\eta \ (\eta = E - E_{eq})$, can be described by the so-called polarization curve.

The polarization curve (as shown for a PEMFC in Fig. 1.2) starts from the open circuit potential (OCP, the potential obtained with zero current), followed by a steep decrease. Subsequently it falls less rapidly till the voltage bends down again more rapidly at higher current density. This way, the polarization curve can be divided into the following regions:

(1) Activation polarization region, where losses in cell voltage are essentially caused by the sluggish kinetics of the electrochemical reactions resulting in an overpotential of ~400 mV [46] at the cathode side (ORR) due to the difficulty in O-O bond breaking (the cathode reaction constitutes the major part of the activation losses), the overall activation loss is the sum of contributions from both anode and cathode side;

(2) Ohmic polarization region, which shows an essentially linear characteristics when currents flow accompanied by a voltage drop (the slop is Volt / Ampere = Ohm) which mainly comes from the resistance of the individual cell components. Furthermore, the slope is sometimes taken as an indicator for estimating the electrolyte resistance. This can be reduced in practical fuel cell systems by using a thin electrolyte with satisfactory mechanical (stability and durability) characteristics as well as a proper cell design.

(3) Mass transport / concentration polarization region, reflects the rapid consumption of reactant at electrode surface.

Generally, the mass transport can be identified as i) migration, which arises from a gradient of electrical potential and causes the movement of charged species, ii) diffusion, which arises from a concentration gradient and causes the movement of a species, iii) convection, which arises from a density gradient (natural convection), e.g., upon stirring or hydrodynamic transport. The concentration polarization results in a gradient between surface ($C_s$) and bulk ($C_b$) reactant concentration. It can be described by the Fick’s first law of diffusion as

$$I = nFD \frac{(C_b - C_s)}{\delta}$$
Figure 1.2 Schematic of typical polarization curve of PEMFC. Activation polarization comes from purely kinetic losses is dominated at low current density region, Ohmic polarization contributed from resistance of ion and electron conduction at medium current density by a nearly linear segment and the Concentration polarization due to onset of reactant transport resistance is facile at high current density. Figure adapted from ref. [10].

where $D$ is the diffusion coefficient and $\delta$ is the thickness of the diffusion layer. In addition, the reactant concentration at the electrode surface depends on the current density. In an extreme case, the surface concentration of reactant approaches zero ($C_s = 0$), which means that the consumption rate constant is faster than the diffusion rate constant. In that case, the overall rate is governed by the mass transfer rate, the corresponding current density under this case is called the limiting current density.

There are great efforts to reduce the overpotential of electrocatalysts. This can be partly achieved by using electrode material with higher intrinsic activity / larger active surface area. In contrast to the promising low anode overpotential observed for pure H$_2$ operation, the presence of trace level of CO ($\sim 10$ ppm), in the hydrogen-rich gas mixture in the fuel of practical H$_2$/O$_2$ fuel cell system leads to a lower power density due to suppressing the H$_2$ oxidation reaction. In this case, the catalyst surface is poisoned by strongly adsorbed CO,
resulting in excessive anode overpotentials. They can be reduced by increased temperature and catalyst loading, or by developing good electrocatalysts with a high activity for H₂ oxidation reaction and CO-tolerance. The challenges in external bulky fuel reforming system, purification and storage of H₂ (high pressure storage, cryogenic storage or hydride storage) [47] strongly drive the motivation for R&D of direct oxidation of small organic molecules (including formic acid, methanol, ethanol, dimethyl ester, ethylene glycol and so on) fuel cells as an alternative approach [48-55], in which the chemical energy of liquid small organic molecules can be directly converted into electrical energy. Direct alcohol fuel cells (DAFC) attracted considerable interest from fundamental and technological point of view due to their high theoretical mass energy density (6.1 and 8.0 kWh kg⁻¹ for methanol and ethanol, respectively), facile liquid fuel storage and simple system structure since they do not require any reforming system, they are promising power sources for portable and mobile applications.

Schematically, the aliphatic alcohol oxidation reaction can be written as follows [56,57],

\[ C_nH_{2n+1}OH + (2n - 1) H_2O \rightarrow nCO_2 + 6 nH^+ + 6 ne^- \]

For DMFC [58] the anodic methanol electrooxidation reaction (CH₃OH + H₂O = CO₂ + 6H⁺ + 6e⁻ E° = 0.016 V_{RHE}) in combination with the cathodic oxygen reduction reaction (3/2O₂ + 6H⁺ + 6e⁻ = 3H₂O, E° = 1.23 V_{RHE}) result in an equilibrium electromotive force of 1.21 V under standard conditions [59].

However, the influence of i) the sluggish reaction kinetics of methanol electrooxidation due to CO_{ad} species formation causes 400–600 mV overpotential at practical current densities, which reduces fuel utilization, ii) Methanol crossover from anode to cathode (due to the concentration gradient related methanol permeability or electro-osmotic drag in the proton conducting membrane, which causes a mixed potential at cathode, iii) mass transport when feeding low concentration of methanol, iv) Ohmic resistance when using thick membrane. Finally, v) flooding at the cathode. In combination, these effects result in a poor performance, specifically output current density and efficiency of DMFCs compared to PEMFC (Fig. 1.2) [60].

In order to improve the kinetics for alcohol electrooxidation, the understanding of reaction mechanism is crucial for further improvement in electrocatalytical activity and optimization
of overall performance. Based on early [61] and recent studies / reviews [52,62-64], methanol electrooxidation reaction involves a complex scheme, which starts from the adsorption of methanol, followed by successive dehydrogenation. This produces three main products: the complete oxidation product of CO\(_2\), and the incomplete oxidation products of formaldehyde (HCHO) and formic acid (HCOOH) [65,66]. The proposed dual pathway mechanism originated from the studies of formic acid oxidation [48,49] and was deduced also for the electrooxidation of methano [50,52, 62,67-69]. Here one pathway proceeds via one or more reaction intermediate (HCOOH, HCHO), followed by conversion to CO\(_2\) [52,70]. The other pathway proceeds via the formation and subsequent oxidation of CO\(_{ad}\). The strong adsorption of CO\(_{ad}\) species formed by dissociative adsorption of methanol increases the overpotential and results in a poor performance. Therefore, the electrooxidation of formaldehyde / formic acid [64,71] and the corresponding understanding of the characteristics of CO adsorption and oxidation (CO + H\(_2\)O→CO\(_2\) + 2e\(^{-}\) + 2H\(^{+}\) in overall reaction process), specifically the oxidative removal of CO\(_{ad}\) species, become indispensable [20,71]. Actually, studies about CO electrooxidation on Pt can trace back to decades ago, when the Langmuir-Hinshelwood (LH) mechanism was introduced as “Gilman’s model” with the suggestion that CO oxidation involves the reaction between adsorbed CO and an electrochemically adsorbed O-containing species. It can be written as:

\[
\begin{align*}
\text{H}_2\text{O} + * & \leftrightarrow \text{OH}_{ad} + \text{H}^{+} + e^{-}, \\
\text{CO}_{ad} + \text{OH}_{ad} & \rightarrow \text{CO}_2 + \text{H}^{+} + e^{-}, + 2* 
\end{align*}
\]

where * stands for a free site on the surface [72]. The interaction of adsorbed CO with the substrate can be ascribed to i) “strongly adsorbed” at low CO\(_{ad}\) coverage and ii) “weakly adsorbed” at high CO\(_{ad}\) coverage, where the substrate-adsorbate interactions are weakened by repulsive CO\(_{ad}\)-CO\(_{ad}\) interactions. The interaction of CO\(_{ad}\) with transition metal surface can be described by the Blyholder model, where the CO\(_{ad}\) orbitals 5\(\sigma\) and 2\(\pi^*\) interact with the localized d metal states forming bonding and anti-bonding hybridized metal-chemisorbate orbitals, which in turn are broadened by the interaction with the much more delocalized sp metal states [73].

To reduce the performance loss from CO\(_{ad}\) “poisoning”, the electrocatalytic properties of platinum can be modified by addition of a second or third metal component to promote CO\(_{ad}\)
oxidation at low potentials. This can be achieved by several effects: i) the bifunctional effect, where the second component promotes the formation of OH$_{ad}$, ii) the ligand effect, where the promoter alters the electronic properties e.g., by reducing the adsorption energy of CO$_{ad}$, iii) the ensemble effect, which is associated with a particular distribution patterns of active constituents [74-76]. Thus, a good electrocatalyst for methanol oxidation reaction should be capable of both dissociative adsorption of methanol molecules and oxidative removal of the resulting chemisorbed fragments by reaction with oxygen containing species, which are supplied by the promotor. Additionally, the development of CO-tolerant electrocatalyst aims at lowering the CO adsorption energy [77-81].

It should be noted that both formaldehyde and formic acid (products of methanol oxidation reaction) can be further oxidized and the corresponding product yield or ratio between them (selectivity) relies strongly on the experimental variables, such as mass transport conditions [82-84], methanol concentration [82-85], flow rate [83], reaction temperature [86,87], composition of the electrode [88-90], catalyst loading [84,91,92], adsorbed anions [93-95] and so on.

Methanol oxidation in alkaline medium [96] is another alternative way to enhance the overall performance. It has significant advantages, such as accelerated methanol oxidation rate due to the higher concentration of hydroxyl species (at high pH electrolyte), facilitating the removal of poisoning ad-species [96,97], and the potential use of non-precious metal catalysts, differs from what is possible in acid medium.

For direct ethanol fuel cells (DEFC), the anodic reaction (CH$_3$CH$_2$OH + 3H$_2$O = 2CO$_2$ + 12H$^+$+12e$^-$, $E^o = 0.085$ V$_{SHE}$) in combination with cathodic oxygen reduction reaction provides an equilibrium electromotive force of about 1.15 V under standard conditions [59]. Though the working principle and operating system of a DEFC is rather similar to that of a DMFC, the DEFC bears some distinct characteristics, such as even higher overpotential, originating from the C-C bond cleavage, and the resulting slower oxidation kinetics, the more complex reaction network with major reaction products acetaldehyde, CO$_2$ and acetic acid, which can not be oxidized further, in contrast to methanol oxidation reaction, where both intermediates (formaldehyde and formic acid) can be oxidized to CO$_2$ [20,54,56,98-103]. This results in more rigid requirements for the anode electrocatalysts, requiring the ability for
complete oxidation of ethanol molecules via C-C bond breaking followed by the removal of the residues formed and strongly adsorbed on the catalyst surface. These demands stimulated studies aiming at more active electrocatalysts and improve of the performance by increasing operation temperature or increasing the pH[104-109]. Other studies focused on a more detailed mechanistic understanding, including verification of adsorbed species, intermediate products and of the corresponding reaction scheme / mechanism (such as reaction pathway, rate determining step).

Engineering challenges (such as the design of bipolar plates, water management, fuel crossover / distribution in the flow field and gas diffusion layer, thickness of membrane electrolyte) in the practical direct ethanol fuel cells render the abovementioned goal far from the realization. This increases the motivation for fundamental model studies performed under more realistic condition, such as more realistic or identical electrocatalysts as used in a practical system rather than single crystals in high vacuum condition, elevated temperature / pressure rather than room temperature / ambient pressure, nevertheless, also under well-fined fuel cell relevant reaction and mass transport condition both in acid and alkaline medium, aiming at further insight into kinetics and mechanism.

1.3 Model studies under fuel cell relevant operating conditions

1.3.1 Model studies on “realistic” electrocatalysts

Realistic fuel cells and corresponding components / systems mainly consist of a membrane electrode assembly (MEA) composed by PEM membrane, catalyst layer made of catalysts mixed with ionomer providing a triple-phase boundary, diffusion layer involving backing layer made of carbon cloth or paper and microporous layer composed of hydrophobic polymer and carbon power, bipolar plates with mechanical flow fields, which definitely involve more technical complexity besides the fundamental consideration of the reaction kinetics, reaction scheme / mechanism [10,110,111]. In order to rule out the influence of the engineering limitations and shed light on the intrinsic kinetics of electrochemical reaction as well as the corresponding mechanism, model studies on polycrystalline and well-defined single crystals in combination with ultrahigh vacuum (UHV) techniques play a key role for
the microscopic interpretation regarding reaction kinetics on atomically clean ordered surface to create a connection between the macroscopic characteristics and the measured activities. Obviously, there are significant difference, between the realistic supported electrocatalyst and the abovementioned model electrodes (even more realistic, massive electrodes), which are termed as the so-called “material-gap” and “pressure-gap” [112,113]. Studies of reaction product / yield of the ethanol oxidation reaction were preformed first on flat electrodes, such as polycrystalline [85,98,99,114-116] and single crystal electrode [117-122], then later on carbon supported nanoparticle electrodes [102,123-127]. This greatly enhanced the opportunity for understanding the intrinsic reaction activity / selectivity, which are closely correlated to the reaction mechanism.

1.3.2 Model studies under well-defined mass transport condition

It is well-accepted that mass transport effect plays an important role in electrocatalysis in general, and also in the electrooxidation of alcohols [128]. A detailed picture of the mass transport effect on the reactivity and selectivity of half-cell reactions (oxygen reduction, methanol oxidation) is described in the “desorption - re-adsorption – further reaction” concept, which was based on mass transport studies over nanostructured Pt/GC model electrodes [45,129-132]. It was shown that variation in Pt nanodisk density and / or in the electrolyte flow rate leads to changes in the reaction activity / selectivity. This mass transport related concept is also valid for the variation of reactant concentration [83,102,133], where an increasing reactant concentration is correlated to an increase in the reactant arrival rate at the electrode surface, resulting in an increasing steady-state coverage of the (re-)adsorbed reaction intermediate. This in turn will influence the reaction characteristic and production distribution.

1.3.3 Model studies at elevated temperature and pressure

In order to improve the electrochemical kinetics, high temperature PEM fuel cells (HT-PEMFC), operating at temperatures above 90°C, have proposed, motivated e.g., by the advantages in simpler water management and cooling [134]. Furthermore, in contrast to
increasing reaction rate by increasing metal loading (resulting in higher cost), increasing temperature represents an “economic” way to increased reaction rates (exchange current density) and enhanced tolerance of the electrocatalyst to contaminants (such as traces of carbon monoxide), favoring desorption of CO at high temperature.

However, the previous model studies on the kinetics and mechanism of the ethanol oxidation reaction were mostly performed at ambient pressure, low temperature (most at room temperature) and in stagnant electrolyte, which is far from the practical fuel cell operation conditions. The significant difference between these conditions stimulated model studies under fuel cell relevant reaction conditions, at specifically elevated temperature and pressure [135-137].

1.3.4 Model studies applying differential electrochemical mass spectrometry (DEMS)

Mass spectrometry (MS), a powerful tool for qualitative and quantitative detection / analysis of products, is performed by monitoring the corresponding mass to charge (m/z) ratio.

Simultaneous or on-line detection and identification of volatile / gaseous electrochemical reaction products / educts by monitoring intensities of the corresponding mass signal during the electrochemical reaction leads to detailed kinetic and mechanistic insight into the ongoing processes. This goal was achieved gradually since the pioneering study of an electrochemical reaction in combination with mass spectrometer, where a painted electrode layer was prepared directly onto a porous Teflon membrane [138]. The time delay between the formation of electrochemical reaction product and the corresponding response of mass spectrometric signal in this approach was about 20 s, which required significant improvement to decrease the time constant to an extent allowing studies of dynamic processes. This was achieved by vacuum sputtering of a metal film directly onto a porous Teflon membrane. Shortening the diffusion path of the volatile / gaseous species between the electrode / solution interface and the mass spectrometer resulted in a fast mass spectrometric response in milliseconds range [139,140]. This technique is therefore named as differential electrochemical mass spectrometry (DEMS), allowing a simultaneous monitoring of the mass signal with the variation of Faradaic current.
(The historical and current development of the technique is presented in detail in reviews [52,141,142].)

However, the approach of thin metal film fabrication directly onto a porous membrane was limited to polycrystalline films of metals and their alloys. The thin-layer cell was developed [143] to overcome these limitations, offering the opportunity of DEMS measurements on massive electrodes, including single crystals, which were positioned directly in front of the bare Teflon membrane by pressing the electrode against a tightener. This results in a microliter electrolyte volume at the working electrode. Therefore the electrolyte in this thin layer cell can be rapidly exchanged, which was utilized for studies of the adsorbate build-up and their oxidation. The latter cell was offering high (close to 100%) collection efficiency in stagnant electrolyte, which, however, drastically decreased for flowing electrolyte. Therefore it is not applicable for studies under continuous reaction / mass transport conditions. The preparation of the electrode layer directly onto the membrane is also not applicable for realistic carbon-supported fuel cell catalysts due to the blocking of pores of membrane with the particles peeled off from electrode (losses of the membrane permeability) and the ill-defined mass transport within the film. An improved design of the thin-layer flow cell was introduced [144], where two interconnected thin-layer compartments served as the components of the common flow reactor, in which the electrochemical reaction products formed at the working electrode in the first compartment are continuously transferred by the flowing electrolyte to the second thin-layer compartment, equipped with a porous membrane interface to the mass spectrometer chamber. In addition to well-defined reaction and mass transport conditions with a reasonable time constant under continuous flow of the electrolyte for the on-line analysis, the dual thin-layer electrochemical interface offers a possibility to adopt different types of working electrodes (from single crystalline massive electrodes to thin-film carbon-supported nanoparticle catalysts), or to change the detector in the second compartment from the membrane inlet to the mass spectrometer for gaseous / volatile products detection to a second electrode for electrochemically active product detection with a high collection efficiency, such as hydrogen peroxide formation in oxygen reduction reaction at the working electrode [45,129,145,146]. Furthermore, combination with different techniques can be achieved using this interface as demonstrated for DEMS and
electrochemical quartz crystal microbalance measurements [144] or an in-situ ATR-FT infrared spectroscopy coupling with DEMS[45,147-149].

1.3.5 Model studies in alkaline medium

The “pH effect” related research originates from the significant problem in direct ethanol fuel cells, including the sluggish kinetics of the oxidation reaction even on platinum and platinum-based electrocatalysts, the high cost of Pt-based electrocatalysts with high precious metal loading to improve the reaction rates; the fast deactivation of the catalyst in acid medium with strong corrosion, which also reduces the lifetime of the whole fuel cell system. As a possible alternative way to overcome the severe problems, ethanol oxidation reaction in alkaline medium was proposed, which results in improved kinetics [105,150-155] compared to that in acidic environment. In particular, it allows the use of less- / non-precious metal electrocatalysts [155-159] as an alternative for Pt-based catalysts. This attracted more and more attention in particular after recent progress in alkaline anion exchange membranes research and development [160-170]. However, the mechanism of the ethanol oxidation reaction on Pt-based and Pd-based catalysts in alkaline electrolyte is still far from being clear and discussed controversially.

1.4 Outline of the thesis

The thesis starts with a brief overview on fuel cells, half-cell reactions and direct small organic molecule oxidation reactions both from a fundamental and from a technical point of view in combination with the general knowledge of electrochemistry / electrocatalysis, which is presented in Chapter 1.

Chapter 2 focuses on the experimental methods including a description and explanation of the differential electrochemical mass spectrometer (DEMS) set-up, the experimental protocol and details of the experiments and evaluation relevant for the understanding of the results.

Chapter 3 [171] reports on model studies on the electrooxidation of ethanol on Pt/Vulcan electrocatalysts at elevated temperature / pressure to gain information on the activity and
selectivity (CO\textsubscript{2} current efficiencies) of the reaction. These studies include potentiodynamic and potentiostatic electrochemical and mass spectrometric measurements under well-defined fuel cell relevant mass transport conditions.

Chapter 4 reports and discusses results of similar model studies on the activity / selectivity of acetaldehyde electrooxidation on a Pt/Vulcan catalyst electrode [172]. Acetaldehyde oxidation is of interest for the mechanistic understanding of the ethanol oxidation reaction, since acetaldehyde is a reactive intermediate in the ethanol electrooxidation reaction. The chapter includes also results on the activity of acetic acid oxidation at high temperatures, which is the second reactive intermediate and was therefore also investigated.

Chapter 5 [173] reports on results of a high temperature / high pressure model study on the electrochemical oxidation of ethanol in alkaline electrolyte on different catalyst electrodes, including Pt-based catalysts (Pt/C, PtRu black) and Pd-based catalysts (Pd/C and Pd/CeO\textsubscript{2}/C). The chapter is based on potentiodynamic and potentiostatic electrochemical measurements performed under fuel cell relevant conditions, under well defined mass transport conditions.

Finally, the main results from the respective chapters are summarized in a coherent picture (in English and German) in Chapter 6.
References


Chapter 2

Experimental
The first section of this chapter is mainly concerned with the experimental setup, which includes (1) an overview of the differential electrochemical mass spectrometer (DEMS) system, (2) a short description of the electrochemical system, including a brief description of the thin-film electrode preparation and the elevated temperature / pressure thin-layer flow cell and its combination with the mass spectrometer.

The second section is comprised of the electrochemical experimental protocols (potentiodynamic and potentiostatic measurements) involved in the present work.

The third part deals with the calibration of the experimental setup and the quantitative evaluation of the resulting data in terms of current efficiency for CO$_2$ formation, for electrooxidation of the investigated model molecules (ethanol and acetaldehyde in acid medium), calculation of apparent activation energies for the overall current and for the partial reaction currents, and finally the active surface area determination via under-potential adsorption of hydrogen and / or adsorbed CO stripping.

Detailed information concerning the electrocatalysts, chemicals and electrolytes used in this work is presented in the last section of this chapter.

### 2.1 Experimental setup

#### 2.1.1 Differential electrochemical mass spectrometer (DEMS) system

As mentioned in 1.3.4, electrochemical measurements in combination with DEMS measurements can supply versatile information on the nature of the electrochemical reaction products. Simultaneous or on-line detection and identification of volatile / gaseous electrochemical reaction products / educts by monitoring the intensities of the corresponding mass signals, during the corresponding electrochemical reaction allows a better kinetic and mechanistic understanding of the ongoing processes.

The DEMS set-up contains two main chambers (the general scheme is shown in Fig. 2.1), which are evacuated by turbomolecular pumps (TMP). The volatile products diffuse through a Teflon membrane into the inlet chamber (pressure of $10^{-3}$ to $10^{-4}$ mbar, pumped by a first TMP).
A small part of the volatile substances enters into the analyzing chamber (pressure ca. $10^{-6}$ mbar, pumped by the second TMP), where the mass analyzer is placed (quadrupole mass spectrometer, Balzers QMS 112).

![Fig. 2.1 Schematic representation of the major configuration of a differential electrochemical mass spectrometer (DEMS). The corresponding abbreviations are represented as: IC = inlet chamber, AC = analyzing chamber, TMP = turbo molecular pumps, RP = roughing pump, QMS = quadrupole mass spectrometer. The electrochemical cell can be connected to DEMS via an open / close valve.](image)

The molecules are ionized by electrons with an electron energy of about 10 eV in the mass spectrometer, the resulting ions are then focused by an electrical optics and accelerated into the quadrupole analyzer, where they are separated based on the m/z ratio. For a specific set of voltage applied to the quadrupole rods, only ions of a given m/z value can pass the quadrupole filter and are detected using a Secondary Electron Multiplier (SEM). The pressures in the two chambers are controlled by a Baratron and a cold cathode gauge, respectively, located in the separate chambers.

### 2.1.2 Electrodes and Electrochemical cell

The thin-film catalyst electrode with negligible diffusion limitations and ca. 100% catalyst
utilization, was prepared according to the procedure described in reference [1]: first, planar glassy carbon rectangular plates (Sigradur G from Hochtemperatur Werkstoffe GmbH, 30 mm × 20 mm × 6 mm) were carefully polished with alumina slurry (down to 0.05 µm grain size). Subsequently, the glass carbon rectangular plates were cleaned by immersion into 5 M KOH for a short time, then rinsed with Millipore Milli-Q water (resistivity ≥ 18 MΩ cm), followed by drying in a nitrogen stream before immersion into concentrated H₂SO₄ for a while. Then the glassy carbon plate was extensively rinsed with Millipore Milli-Q water and dried in the N₂ stream.

Fig. 2.2 Foto of the high temperature / high pressure (HT / Hp) DEMS cell (upper panel) and a schematic drawing (see text).
The circular thin-film electrodes, including Pt/Vulcan (20 wt% metal, E-TEK Inc.), Pd/C (5 wt% metal, Degussa), Pd/CeO$_2$/C (10 wt% metal, Hypermec Acta) and PtRu black (Pt:Ru = 1:1 in atomic ratio, Johnson Matthey) catalysts, were prepared in the middle of the pre-cleaned rectangular glassy carbon substrates, following the procedure described in ref.[1], by pipetting and drying 20 $\mu$L of an ultrasonically re-dispersed aqueous catalyst suspension (for details see part 2.4) and then pipetting 20 $\mu$L of aqueous Nafion solution and drying in a mild nitrogen stream. This produces a Nafion film of ca. 0.1 µm in thickness over the catalyst film, which ensures the physical stability of the catalyst layer and does not introduce significant diffusion resistance [1]. The resulting thin catalyst film had a diameter of ca. 5 mm, a geometric surface area of 0.2 cm$^2$ (detailed information for the respective catalyst loadings is given in part 2.4).

The electrochemical high temperature / high pressure (HT / Hp) thin-layer channel flow cell had been described and characterized in terms of its mass transport pattern recently [2]. It was used for the HT/HP DEMS measurements [3-5] as shown in Fig. 2.2. The thin-layer flow cell has well-defined hydrodynamic characteristics and allows operation at up to 100 °C and 3 bar overpressure. It is composed of a chemically inert and physically resistant polymer (PolyEtherEtherKetone - PEEK) cell body with a Pt wire counter electrode located in a separate compartment of the cell body behind the circular glass frit directly in front of the working electrode. A by-pass for the electrolyte (see Fig. 2.2) helps to remove the gas bubbles formed at the counter electrode.

The rectangular flow channel (8 × 12 mm) was surrounded by a pre-cut, 50 µm thick polymer film gasket (20 × 30 mm, fluorinated ethylene-propylene - FEP, Bohlender), which is placed between cell body and glassy carbon plate and positioned by four stainless steel guidance rods. A well-defined electrolyte flow rate was ensured by the pressurised (3 bar overpressure) electrolyte supply bottles, which were connected to the inlet of the thin-layer cell, and a pressure resistant syringe pump, connected to the outlet of the cell. The cell is ionically connected to the external reference electrode (saturated calomel electrode-SCE) via a Luggin capillary at the inlet of the cell.

The electrochemical measurements were performed using a Pine Instruments potentiostat (model AFRDE5) and a computerized data acquisition system.
2.1.3 Interfacing the high pressure / high temperature electrochemical flow cell to the mass spectrometer

The hydrophobic porous Teflon membranes, which are commonly used in DEMS applications, allow dissolved gaseous or other volatile species (including water) to evaporate through the pores [6,7] and enter the differentially pumped mass spectrometer chamber [8,9], while liquid water can not penetrate through it. As reported in reference [10], the critical pore size is defined the surface tension of water and the contact angle between water and Teflon, which results in a critical pore diameter of \( r < 0.8 \mu m \). At elevated pressure and temperature conditions, a conventional porous membrane interface would result in extensive evaporation of water and volatile organic molecules into the vacuum chamber. Therefore, a membrane interface with lower permeability must be used to reduce the water vapor pressure in the vacuum system. A 10 \( \mu m \) thick low porosity Teflon film was employed in present study, which is sufficiently permeable for gases, while on the other hand, it can efficiently suppress the evaporation of water and volatile organic species into the vacuum chamber. The membrane is also not permeable for larger molecules, which was successfully utilized in the present study to avoid evaporation / ionization of ethanol and acetaldehyde and the resulting interference of different products / fragments with mass number 44 and CO\(_2\) [3]. The thin membrane interface was supported by a stainless steel frit and installed in a separate circular thin-layer flow cell module fabricated from Kel-F. The inlet of the latter module was connected to the outlet of the thin-layer electrochemical cell via a capillary, while the outlet of the membrane interface unit was connected to the syringe pump (details see Fig. 2.3). If not necessary (measurements in alkaline solution, where the carbon dioxide is readily converted to carbonate and thus cannot be detected by DEMS), the membrane interface unit was skipped and only performing for electrochemical HT / Hp measurements.

The whole setup and connection between HT / Hp thin layer flow cell set up and DEMS is shown in Fig. 2.3. First the electrolytes (such as base / supporting electrolyte of 0.5 M H\(_2\)SO\(_4\) or 0.5 M NaOH, model molecules containing electrolyte and 0.1 M formic acid containing electrolyte for calibration) are pressurized via the gas line (3 bar Ar or N\(_2\) overpressure) and kept in tightly closed supply bottles, which are located in the commercial thermostat (Lauda E200), where they can be heated to the desired temperature. The electrolyte is supplied from
the pressurized glass bottles via PEEK capillaries and an inert, high temperature / high pressure multi-port valve to the high temperature / high pressure thin-layer flow cell, which is located in a home-built air thermostat controlled by a temperature program unit. The flow cell is connected via a PEEK capillary to the second thin-layer compartment, which contains a non-porous Teflon membrane interface to the mass spectrometer, and finally connected via a capillary to the pressure-resistant syringe pump (Harward Apparatus 11plus) for the flow rate control.

Fig. 2.3  Schematic description of the combined high temperature / high pressure (HT/HP) thin-layer flow cell / DEMS setup. Upper panel: A: Gas line, B: Thermostat (Lauda E200), C: Glass supply bottle, D: Inert multiport valve, E: home made air thermostat (HT / Hp flow cell was placed inside) F: Saturated calomel electrode (including the port), G: Teflon open/close valve (connected to the counter electrode), H: Second (detector) compartment, I: Temperature program controller (for the home made thermostat), J: Pressure resistant syringe pump (Harward Apparatus 11 plus). Bottom panel: Second (detector) compartment for combination of electrochemical cell and DEMS: the inlet is connected to the outlet of the electrochemical cell, and the outlet is connected to the syringe pump.
The reference electrode is connected to the valve located between the outlet of the high temperature/ high pressure multi-port valve and the inlet of the high temperature / high pressure thin-layer flow cell. The connection consists of a PEEK capillary with a Teflon open / close valve for rinsing. It leads to an external saturated calomel electrode (SCE), which is operated at ambient temperature.

It should be noted that for acetaldehyde electrooxidation the experimental set-up has been modified because of its low boiling point (b.p. 21 °C). Here, the electrolytes were supplied from pressurized glass bottles thermostated separately, while the acetaldehyde containing stock solution was kept at room temperature.

This modification was necessary to minimize losses of acetaldehyde due to evaporation. The supporting electrolyte was first thoroughly deaerated by purging N₂, and then acetaldehyde was added to the desired concentration. Subsequently, the electrolyte was shortly purged again, pressurized with N₂ in the supply bottle, which was kept at room temperature, and then connected to a separate 50 mL glass reservoir, which was located in the
air thermostat box directly before the flow cell and pre-filled with the same deaerated acetaldehyde solution (kept at room temperature). Keeping a constant level of acetaldehyde solution in the hot reservoir, we could maintain a constant concentration of acetaldehyde in the hot electrolyte during reaction. Otherwise, the acetaldehyde concentration decayed rapidly with increasing gas phase volume in the heated supply bottle due to evaporation into the increasing gas volume. It should be noted that the volume of the 50 mL glass reservoir is big enough for skipping the possible influence of the thermal distribution or temperature variation for the electrolyte inside the glass reservoir during the continuous electrolyte flow (flow rate of 15 µL/s), which was controlled by a pressure-resistant syringe pump.

2.2 Experimental protocol

The main methods used in the studies of electrochemical oxidation reaction in the present contribution, potentiodynamic and potentiostatic measurements, are briefly introduced in the following part.

2.2.1 Potentiodynamic measurements - Cyclic Voltammetry (CV)

As described in the book of “Electrochemistry” [11], “cyclic voltammetry involves the imposition of a triangular waveform as the potential on the working electrode with the simultaneous measurements of the current”, cyclic voltammetry (current-potential profiles) acts as a versatile tool for the analysis of the current response when a cyclic potential sweep is imposed on the electrode. This provides fruitful information on the thermodynamics and kinetics of electron transfer at the electrode / electrolyte interface. The procedure for cyclic voltammetry in the present work is shown in Fig. 2.5, with a potential scan rate of 10 mVs$^{-1}$ in the potential range of 0.06 V ~ 1.16 V. The cycle starts at the region of hydrogen evolution and reaches till the oxygen evolution region, which has the advantage that impurities on the electrode surface can be removed by cyclic reduction or oxidation. Actually, in the present work, the upper positive limit for Pt/Vulcan electrodes was set to below 1.2 V to avoid a possible electrooxidation of the carbon support and to 0.8 V for the PtRu black catalyst to prevent a possible electrochemical dissolution of the Ru component at higher potentials.
According to the direction of potential sweeping, the cyclic voltammograms can be divided into a positive-going scan and negative-going scan (as shown in Fig. 2.5).

\[ E = E_i + vt \quad \text{(positive-going scan)} \]
\[ E = E_s - vt \quad \text{(negative-going scan)} \]

**Fig. 2.5** Schematic representation of potentiodynamic procedure. E\textsubscript{i}: initial potential, E\textsubscript{s}: switching potential, where the sweeping direction changed and E\textsubscript{f}: final potential, \( v \): scan rate

In the present contribution, the cyclic voltammograms and the corresponding mass-spectrometric signal from DEMS measurements are obtained. They reveal the influence of concentration, potential and temperature on the activity and selectivity (CO\textsubscript{2} current efficiency) for ethanol oxidation (chapter 3) and acetaldehyde oxidation (chapter 4) as well as the activity of ethanol oxidation reaction on different electrodes in an alkaline environment (chapter 5).

### 2.2.2 Potentiostatic measurements – Chronoamperometry

*Chronoamperometry* belongs to the general step techniques, involving the measurement of the Faradaic current as a function of time after applying a potential step perturbation. In a typical potential-step measurement, the applied potential “step” from the initial value to the respective reaction potential leads to both double-layer charging and conversion of the
adsorbed reactant on the electrode surface, which results in a sharp “spike” (dominated by pseudo-capacitive contributions). The experimental protocol for potentiostatic measurements in the present work is shown in Fig. 2.6 (upper panel) and can be described as follows: the negative-going potential scan was stopped at 0.06 V prior to the constant potential measurements, held there for 5 minutes. Subsequently, the potential was stepwise increased, first to 0.18 V for ethanol oxidation in 0.5 M H$_2$SO$_4$ and 0.2 V for other measurement, and then by increments of 0.1 V to higher potentials. Each potential was held for 5 min, except for the highest potential of 0.68 V for ethanol oxidation in 0.5 M H$_2$SO$_4$ because of the onset of bubble formation. Finally, the potential was stepped back to 0.06 V, holding at this potential until the background signal of the $m/z = 44$ ion current was sufficiently stable for proper background drift correction (for the measurement in acid medium).

The same protocol was used also for studying ethanol oxidation in alkaline solution on different electrodes: stepping from an initial potential of 0.06 V succeeding to the respective potential (holding for 5 min), followed by stepping back to 0.06 V (upper panel, Fig. 2.6).
Fig. 2.6  Schematic representation of potentiostatic protocol: upper panel: “standard” potentiostatic protocol with 5 min for each step, bottom panel: long-term procedure for potentiostatic ethanol oxidation on Pt/Vulcan in 0.5 M 0.1 M EtOH and 0.5 M NaOH solution with 15 min for each step at potential range from 0.4 to 0.7 V.

However, it should be noted that for the ethanol oxidation reaction on Pt/Vulcan catalyst in alkaline solution, which at potentials of 0.4 and 0.5 V appeared to be severely affected by the “history” of the previously applied potentials, a different experimental protocol was applied, in order to obtain a well defined initial electrode state (bottom panel, Fig. 2.6). This included:

i)  pre-cleaning of the electrode by stepping from 0.06 to 1.2 V (20s) to oxidatively remove adsorbed residues,

ii)  stepping back to 0.06 V (60s) to protect the electrode surface from the dissociative adsorption of ethanol by underpotentially adsorbed hydrogen,

iii) stepping to the desired potential (between 0.4 and 0.7 V). A prolonged time of 15 minutes was used for each potential step for reaching steady-state currents.

In order to extract the influence of capacitive contributions, a series of experiments were performed on Pt/Vulcan catalyst in ethanol free 0.5 M supporting NaOH electrolyte under analogous experimental conditions, where the initial current spike solely consists of capacitive contributions.

2.3 Calibration / evaluation

This section contains the following parts: i) the calibration of the reference electrode at the respective temperatures, ii) the calibration of the mass spectrometer and the quantitative data evaluation, iii) the calculation of the apparent activation energies, and iv) the electrochemically active surface area determination.

2.3.1 Calibration of reference electrode

The calibration of the saturated calomel electrode (SCE) reference electrode, operated at ambient temperature, versus a reversible hydrogen electrode (RHE) at the respective temperature, required separate experiments to determine the onset of the hydrogen oxidation /
evolution reaction (HOR / HER) on a similar Pt/Vulcan electrode in the supporting electrolyte under a constant hydrogen overpressure of 3 bar at various temperatures (from 23 to 100°C) and the same flow rate of 15 µLs⁻¹.

The resulting potential of zero-current (crossing point) at the respective temperatures (Fig. 2.7) corresponds to the reversible hydrogen electrode potential under the applied conditions. This was used for the conversion of the SCE scale to that of the RHE.

**Fig. 2.7** Hydrogen oxidation / evolution reaction on a Pt/Vulcan catalyst (20 wt%, E-tek) for calibration of the saturated calomel electrode at different temperatures from 23 to 100°C in H₂-saturated (3 bar overpressure) 0.5 M H₂SO₄ supporting electrolyte at a flow rate of 15 µLs⁻¹.

The calibration of the saturated calomel electrode vs. the reversible hydrogen electrode in alkaline solution (not shown) was performed in the same way on a Pt/Vulcan electrode in 0.5 M NaOH solution under 3 bar overpressure of H₂ at the same flow rate of 15 µLs⁻¹. All potentials in the present work are quoted against that of a reversible hydrogen electrode (RHE) in both acid and alkaline media.
2.3.2 Calibration of electrooxidation reaction in acid solution

As mentioned above in section 2.1.3, the use of a non-porous Teflon membrane with a low permeability for keeping the water vapor level at tolerable levels, especially, at high temperatures and high pressure, inhibits the permeation of larger molecules such as acetaldehyde or ethanol. This enabled us to monitor the CO$_2$ partial pressure via the $m/z = 44$ signal without interference with the acetaldehyde signal (also at $m/z = 44$). The absence of acetaldehyde vapor in the mass spectrometer chamber was confirmed by the absence of any features in the $m/z = 29$ ion current (CHO$^+$ fragment of acetaldehyde) as a function of the potential. Furthermore, we found no change in the background level at the $m/z = 44$ signal when changing from supporting electrolyte to a pressurized (3 bar overpressure) 0.01 M acetaldehyde solution at all temperatures. Finally, the ion current at $m/z = 22$ (doubly ionized CO$_2^{2+}$; 2.8% of the main $m/z = 44$ CO$_2$ peak [12]), which was also recorded in all experiments, was found to quantitatively agree with the $m/z = 44$ signal. Therefore, in the present work, we will only show the $m/z = 44$ signal, because of its much better signal-to-noise (s / n) ratio.

2.3.3 Determination of the calibration constant $K_{44}^*$ and the partial currents for complete oxidation to CO$_2$

The calibration constant $K_{44}^*$ ($m/z = 44$) was determined by potentiostatic HCOOH bulk oxidation at the respective temperatures. $K_{44}^*$ was obtained via the relation:

$$K_{44}^* = 2 \frac{I_{MS}(m/z = 44)}{I_F}$$

(2.3.1)

where $I_F$ is the Faradaic current during HCOOH bulk oxidation, $I_{MS}(m/z = 44)$ is the mass spectrometric current and 2 is the number of electrons needed for formation of one CO$_2$ molecule from HCOOH. To remove effects from the temperature dependent permeability of the membrane, the CO$_2$ related $m/z = 44$ signals were normalized to the $K^*$ value at room temperature, which were determined as reference before each series of measurements. The time delay between onset of Faradaic current and the corresponding ion signal, which is caused by the finite time required for the electrolyte flow from the first to the second (detector) compartment (~4 s at a flow rate of 15 µL s$^{-1}$ at the present length of the capillary connection between HT/HP flow cell and membrane inlet), was corrected accordingly.
The equation for complete electrooxidation of ethanol in 0.5 M H$_2$SO$_4$ is

$$\text{CH}_3\text{CH}_2\text{OH} + 3 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 12 \text{e}^- + 12 \text{H}^+ \quad (2.3.2)$$

The partial current for complete ethanol electrooxidation to CO$_2$, $I_p$(CO$_2$), was calculated using the following equation:

$$I_p(\text{CO}_2) = 6 \frac{I_{MS}(m/z = 44)}{K^{*}_{44}} \quad (2.3.3)$$

where $I_{MS}(m/z = 44)$ is the mass spectrometric current of the $m/z = 44$ signal, the factor of 6 reflects the average number of electrons needed for formation of one CO$_2$ molecule per C atom in ethanol and $K^{*}_{44}$ is the calibration constant for $m/z = 44$, determined by potentiostatic HCOOH bulk oxidation at the respective temperatures, from 23 to 100 °C, on a Pt/Vulcan catalyst as described above.

The corresponding evaluation of the current efficiency for CO$_2$ formation was performed by calculating the ratio of the partial current for ethanol oxidation to CO$_2$ (see eq. 2.3.3), $I_p$(CO$_2$), and the overall Faradaic current ($I_F$) for ethanol oxidation.

The corresponding equation for complete acetaldehyde electrooxidation reaction is

$$\text{CH}_3\text{CHO} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 10 \text{H}^+ + 10 \text{e}^- \quad (2.3.4)$$

The partial current for complete acetaldehyde electrooxidation to CO$_2$, $I_p$(CO$_2$), was calculated using the following equation:

$$I_p(\text{CO}_2) = 5 \frac{I_{MS}(m/z = 44)}{K^{*}_{44}} \quad (2.3.5)$$

where $I_{MS}(m/z = 44)$ is the mass spectrometric current of the $m/z = 44$ signal, the factor of 5 represents the average number of electrons needed for formation of one CO$_2$ molecule per C atom in acetaldehyde, and $K^{*}_{44}$ is the calibration constant for $m/z = 44$ (determination see above).

The corresponding current efficiency for CO$_2$ formation was thus calculated by the ratio of $I_p$(CO$_2$) / $I_F$.

The equation for complete electrooxidation of acetic acid is

$$\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^- \quad (2.3.6)$$
Because of the very small rates for acetic acid oxidation, the Faradaic current and corresponding ion current at \( m/z = 44 \) were corrected for additional contributions, which may arise, e.g., from oxidation of the carbon support, by subtracting the respective currents measured in acetic acid free supporting electrolyte.

### 2.3.4 Calculation of apparent activation energies

According to the Arrhenius plots of the logarithmic oxidation rate against the inverse temperature (\( \ln i \sim 1/T \)), the apparent activation energies were calculated for the rate of complete ethanol oxidation to \( \text{CO}_2 \) (\( I_{\text{F}}(\text{CO}_2) \)) and the total Faradaic currents (\( I_{\text{F}} \)), respectively, from steady-state currents during potentiostatic ethanol oxidation. Similarly, the apparent activation energies for acetaldehyde oxidation to \( \text{CO}_2 \), incomplete oxidation of acetaldehyde to acetic acid (calculated from the difference between the total reaction current and the partial reaction currents of complete oxidation to \( \text{CO}_2 \)) as well as complete oxidation of acetic acid to \( \text{CO}_2 \) were also calculated in the same way.

Because of the limitations of the experimental method in alkaline solution (absence of combination to DEMS due to carbonate or bicarbonate formation), only the apparent activation energies for overall oxidation reaction rate were obtained from steady-state currents. It should be noted that the corresponding apparent activation energies for Pt/Vulcan at 0.4 and 0.5 V were calculated from the double-layer charging corrected initial currents rather than from the steady-state currents, mainly due to the observations that the steady-state currents at the highest temperature(s) deviated significantly from a linear \( \ln i \) vs. \( 1/T \) relation and that the resulting apparent activation energies differed strongly from the values obtained at higher potential (for discussion see section 5.2.4).

### 2.3.5 Electrode active surface area determination

Before each measurement, the cell was carefully flushed with supporting electrolyte, then the thin-film electrode was cycled in the potential range between 0.06 and 1.16 V (100 mV s\(^{-1}\) scan rate), until the cyclic voltammograms for a clean Pt/Vulcan electrode was reproduced [13]. The \( \text{H}_{\text{upd}} \) charge was used as an inherent reference to check for possible losses of
catalyst after each experiment. In more detail, the amount of the electric charge related to the 
$H_{\text{upd}}$ uptake / desorption at potentials between 0.06 and 0.36 V after subtracting the double-
layer charging contribution on Pt is taken for determining the electrochemically active surface 
area ($S_{\text{ECSA}}$) [14]. From the $H_{\text{upd}}$ adsorption charge in the base cyclic voltammetry (CV), the 
electrochemically active surface area was estimated based on assuming that the $H_{\text{upd}}$ coverage 
at the onset of bulk hydrogen evolution is 0.77 monolayers (ML) [15] and that the hydrogen 
monolayer adsorption charge on polycrystalline Pt is equal to 0.21 mC/cm$^2$ [16], resulting in 
the relation:

$$S_{\text{ECSA}} = \frac{Q_{H\text{-upsd}}}{0.77 \text{ ML} \times 0.21 \text{ mC/cm}^2 \cdot \text{ML}}$$

(2.3.7)

where $Q_{H\text{-upsd}}$ is the integrated charge for hydrogen underpotential deposition.

Similarly, in alkaline solution, prior to each measurement, the cell was carefully flushed 
with the supporting electrolyte, then the thin-film electrode was cycled in the potential range 
between 0.06 and 1.16 V for the Pt/C and Pd/C catalysts, from 0.06 to 0.8 V for the PtRu 
black catalyst and in the range of 0.1– 1.2 V for the Pd/CeO$_2$/C catalyst (all at 100 mV s$^{-1}$ 
scan rate), until the cyclic voltammogram of a clean electrode was reproduced.

The corresponding active surface area of the Pt/Vulcan catalyst was estimated with the 
same procedure and equation (equation 2.3.7), however, the corresponding ECSA used for 
evaluation of the specific activity was obtained by means of oxidizing pre-adsorbed CO$_{\text{ad}}$ 
monolayers (CO$_{\text{ad}}$ stripping) because of the ill-defined hydrogen desorption / adsorption 
characteristics for the other electrodes (PtRu black, Pd/C and Pd/CeO$_2$/C) in alkaline solution.

Because the formation of (bi)carbonate in the aqueous alkaline electrolyte, which can not 
penetrate through the membrane, greatly hampered the application of DEMS for the study of 
the reaction selectivity (CO$_2$ current efficiency) for ethanol oxidation reaction in alkaline 
solution, the study of ethanol oxidation in alkaline solution (section 5) was limited to 
electrochemical measurements of the respective activity of different Pt-based and Pd-based 
catalyst electrodes as well as of the temperature / potential dependent characteristics of the 
mass specific and electrochemically active surface area specific activities.

The mass (specific) activities, where the Faradaic currents are normalized by the respective 
mass of the Pt or Pd component on the electrode, are determined by using the following
masses of noble metal on the electrode: 2 \( \mu g_{Pt} \) for the Pt/C catalyst, 13.2 \( \mu g_{Pt} \) for the PtRu black catalyst, 8 \( \mu g_{Pd} \) for the Pd/C catalyst and 8 \( \mu g_{Pd} \) for the Pd/CeO\(_2\)/C catalyst, respectively.

The electrochemically active surface area (ECSA) of the respective electrodes in alkaline medium were obtained from CO stripping measurements (as shown in Fig. 2.8) performed in a three electrode beaker cell at room temperature on an electrode pre-cleaned by fast potential cycling followed by pre-adsorption of CO at a constant electrode potential (0.2 V) for 10 min. Then the cell was purged by Ar for half an hour for removing the remaining CO in the electrolyte (0.5 M NaOH solution) at the same electrode potential. Finally, the CO adlayer was oxidatively stripped at a potential scan rate of 10 mV s\(^{-1}\) and the second potential cycle of the CO\(_{ad}\)-free electrode was also recorded for comparison.
Fig. 2.8 Voltammetric profiles for CO stripping on (a) Pt/C, (b) PtRu black, (c) Pd/C and (d) Pd/CeO$_2$/C catalysts in a three-electrode beaker cell after CO adsorption for 5 min (potential scan rate 10 mV s$^{-1}$, starting with a negative scan from the adsorption potential to the cathodic potential limit followed by two full potential cycles).

The resulting active surface areas for the normalization of EOR activities are as follows, 4.38 cm$^2$ for the Pt/C catalyst, 3.76 cm$^2$ for the PtRu black catalyst, 7.76 cm$^2$ for the Pd/C catalyst and 5.99 cm$^2$ for the Pd/CeO$_2$/C catalyst.

### 2.4 Electrocatalysts and Chemicals

The supporting electrolyte was prepared using Millipore Milli-Q water and suprapure sulfuric acid (suprapur), Ethanol (LiChrosolv), formic acid (Guaranteed Reagent, GR), acetic acid (GR) and NaOH pellets (GR for analysis) were obtained from Merck and acetaldehyde ($\geq$ 99.5 %, ACS reagent) from Sigma-Aldrich.

All solutions used for ethanol, acetaldehyde and acetic acid oxidation in 0.5 M H$_2$SO$_4$ solution were deaerated by high-purity Ar (MTI Gase, N6.0, from Messer-Griesheim), those used for ethanol oxidation in alkaline medium were deaerated by N$_2$.

The electrocatalysts used in this work are listed in the following table.
Table 2.1 Description of the respective catalysts and thin-film electrodes
(catalyst suspension, metal loading of the electrode).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal loading</th>
<th>Suspension</th>
<th>Metal loading on electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt / Vulcan</td>
<td>20 wtPt %</td>
<td>2 mg/mL</td>
<td>40 µg/cm² (*)</td>
</tr>
<tr>
<td>(E-Tek)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt / Vulcan</td>
<td>20 wtPt %</td>
<td>0.5 mg/mL</td>
<td>10 µg/cm² (**)</td>
</tr>
<tr>
<td>(E-Tek)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd / C</td>
<td>5 wtPd %</td>
<td>8 mg/mL</td>
<td>40 µg/cm² (**)</td>
</tr>
<tr>
<td>(Degussa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd / CeO₂ / C</td>
<td>10 wtPd %</td>
<td>4 mg/mL</td>
<td>40 µg/cm² (**)</td>
</tr>
<tr>
<td>(Hypermec Acta)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| PtRu black     | Pt:Ru = 50:50 atom % | 1 mg/mL | Pt: 66 µg/cm² (**)
| (Johnson Matthey)|             |            | Ru: 34 µg/cm²              |

(*) Electro catalyst for the study on ethanol, acetaldehyde and acetic acid electro-oxidation in acidic medium (0.5 M H₂SO₄)

(**) Electro catalysts for the study of ethanol electro-oxidation in alkaline solution (0.5 M NaOH).
2.5 References


Chapter 3

Ethanol electrooxidation on Pt/C catalyst at elevated temperature and pressure in acid medium: A HT / Hp DEMS Study
The content of the following section is extracted from an article by S. Sun, M. Chojak Halseid, M. Heinen, Z. Jusys, and R.J. Behm, “Ethanol electrooxidation on a carbon-supported Pt catalyst at elevated temperature and pressure: A high-temperature/high-pressure DEMS study”, which has already been published in the Journal of Power Sources (190, 2-13, 2009). It is adopted with permission from Elsevier, © 2009. The corresponding figures and tables have been adapted to fit the layout of the thesis. The experimental description for the following section is summarized in the Experimental part in Chapter 2. The figures, tables and the corresponding descriptions involved in the following section are same as published. The majority of the data acquisitions, evaluation, graphing and writing of the manuscript were done by the author of this thesis.

Abstract

The electrooxidation of ethanol on a Pt/Vulcan catalyst was investigated in model studies by on-line differential electrochemical mass spectrometry (DEMS) over a wide range of reaction temperatures (23 – 100°C). Potentiodynamic and potentiostatic measurements of the Faradaic current and the CO$_2$ formation rate, performed at 3 bar overpressure under well-defined transport and diffusion conditions reveal significant effects of temperature, potential and ethanol concentration on the total reaction activity and on the selectivity for the pathway toward complete oxidation to CO$_2$. The latter pathway increasingly prevails at higher temperature, lower concentration and lower potentials (~90% current efficiency for CO$_2$ formation at 100°C, 0.01 M, 0.48 V), while at higher ethanol concentrations (0.1 M), higher potentials or lower temperatures the current efficiency for CO$_2$ formation drops, reaching values of a few percent at room temperature. These trends result in a significantly higher apparent activation barrier for complete oxidation to CO$_2$ (68±2 kJ mol$^{-1}$ at 0.48 V, 0.1 M) compared to that of the overall ethanol oxidation reaction determined from the Faradaic current (42±2 kJ mol$^{-1}$ at 0.48 V, 0.1 M). The mechanistic implications of these results and the importance of relevant reaction and mass transport conditions in model studies for reaction predictions in fuel cell applications are discussed.
3.1 Introduction

Direct ethanol fuel cells (DEFCs) have received growing attention as renewable power sources during recent years [1-8]. The successful introduction of DEFCs is hindered, however, by the slow kinetics of the ethanol electrooxidation reaction and its poor selectivity toward complete oxidation to CO$_2$ [6,9-16], while much or even most of the ethanol is only partly oxidized to acetaldehyde or acetic acid (see below). The kinetics and mechanism of the ethanol oxidation reaction (EOR) have been investigated extensively in model studies on massive electrodes and supported catalysts electrodes, employing purely electrochemical measurements as well as *in-situ* spectroscopic techniques (for a summary see below). Direct transfer of these results to the reaction in a realistic fuel cell, however, is hardly possible because of the very different reaction and mass transport conditions in both cases: While DEFCs are operated at elevated temperatures under enforced electrolyte transport, using high surface area electrodes, model studies are mostly performed at room temperature and in stagnant electrolyte, in the absence of enforced electrolyte transport, and often on massive metal electrodes with low surface area (for reviews see [17,18]). Detailed reaction studies performed using realistic fuel cells, on the other hand, are rare [6,9,14,15,19,20], and the reaction conditions are much less defined than those in model studies and may differ significantly between different studies. For instance, measurements of the CO$_2$ product yield and CO$_2$ current efficiency, which were performed in three different studies [6,9,19,20], arrived at widely differing results. Measuring the relative product distribution for ethanol oxidation at the exhaust of a polybenzamidazole (PBI) fuel cell by on-line mass spectrometry (temperature range 150 - 190°C), Wang et al. determined acetaldehyde as the main reaction product and CO$_2$ as a minority product, with the CO$_2$ content increasing with increasing water-to-ethanol ratio [9]. On the other hand, Aricò et al. reported a high selectivity toward CO$_2$ formation (95%) for ethanol oxidation in a liquid-feed polymer electrolyte fuel cell with a PtRu/Vulcan anode catalyst (145°C, 1 M ethanol) [19]. Comparable results were published by Rao et al. for ethanol oxidation over a Pt/C catalyst, who measured the CO$_2$ concentration at the exhaust of a DEFC by on-line mass spectrometry in the temperature range between 30 and 90°C and obtained a current efficiency for CO$_2$ formation of more than 75% at 90°C (0.1
M ethanol, 5 mg/cm\(^2\) Pt catalyst loading), whereas for 1 M ethanol oxidation on a PtRu/C catalyst MEA the current efficiency for CO\(_2\) formation was significantly lower [20].

Comparable model studies, which were performed at room temperature in stagnant electrolyte, also led to diverging results on the product distribution [11,12,21,22]. Hitmi et al. determined acetic acid as main product for ethanol oxidation on polycrystalline Pt at 10°C / 0.8 V at low concentrations (<0.01 M), whereas acetaldehyde prevailed at high concentration (>0.1 M) [21]. In contrast, much higher relative yields of CO\(_2\), reaching even 100%, were determined by on-line differential electrochemical mass spectrometry (DEMS) for ethanol oxidation on PtRu electrodes at low temperatures (5 and 25°C) [22]. On the other hand, rather low current efficiencies for CO\(_2\) formation were obtained in model studies over PtRu and PtRu/C catalysts [23-26]. Without commenting on the very different results of these model studies, it is clear that the reaction conditions are incommensurable with those in fuel cell measurements. Recently, Wang et al. systematically investigated the product distribution of ethanol oxidation over a Pt/Vulcan catalyst as a function of temperature (23 - 60°C), ethanol concentration and catalyst loading in a model study by DEMS, using a thin-film supported catalyst (Pt/Vulcan) electrode with negligible diffusion resistance and well defined enforced electrolyte mass transport [10]. Incomplete ethanol oxidation to acetaldehyde and acetic acid was found to prevail over complete oxidation to CO\(_2\) under these experimental conditions, with CO\(_2\) current efficiencies in the range of a few percent at most.

To further approach the situation in a realistic fuel cell, while maintaining the well defined reaction and transport conditions in model studies, it is particularly important to raise the reaction temperature to at least 100°C, possibly even higher, which also requires pressurizing the reaction cell and the electrolyte to prevent evaporation of electrolyte and reactants. A number of groups reported the build-up of pressurized high-temperature cells [27-37]. These cells allow operation at relevant temperatures, mostly also under controlled and enforced electrolyte transport, but are limited to purely electrochemical measurements.

Recently, we developed a high-temperature/high-pressure DEMS set-up which allows electrocatalytic measurements on supported catalyst thin-film electrodes (ca. 100% catalyst utilization, negligible diffusion limitations) at elevated temperatures (up to 100°C) and pressure (3 bar overpressure) under continuous reaction and well defined, enforced mass transport.
conditions. [38]. This set-up was employed to investigate the electrooxidation of ethanol on carbon supported Pt/Vulcan catalysts at temperatures up to 100°C under well defined and fuel cell relevant reaction and transport conditions. Although from experimental reasons we cannot discriminate between acetaldehyde and acetic acid product formation at present (see Chapter 2, Experimental part), this allows us to discriminate between partial oxidation (acetaldehyde, acetic acid formation) and complete oxidation (CO₂ formation), which is particularly interesting for practical applications. Preliminary results of this study were published recently [38].

In the following we will, after a brief description of the experimental set-up and procedures (section 3.2), first present and discuss results of potentiodynamic (section 3.2.1) and potentiostatic (section 3.2.2) measurements in 0.1 M and 0.01 M ethanol solutions, covering the wide temperature range between ambient temperature and 100°C. The data are used to evaluate the current efficiency for the complete oxidation of ethanol to CO₂ under different conditions, and to calculate the apparent activation energies for the overall ethanol oxidation and for complete oxidation to CO₂ at different potentials (section 3.2.3). Finally, the mechanistic and kinetic implications arising from these data as well as the importance of realistic reaction conditions in model studies for the prediction of the reaction behavior in fuel cells will be discussed.

3.2 Results and discussion

3.2.1 Potentiodynamic oxidation of ethanol on a Pt/Vulcan catalyst

Fig. 3.1 shows a series of potentiodynamic DEMS measurements of the ethanol electrooxidation reaction over the Pt/Vulcan catalyst in 0.1 M ethanol containing 0.5 M H₂SO₄ solution at different temperatures (23, 40, 50, 60, 70, 80, 90 and 100°C). (Note that the Faradaic current was corrected for pseudo-capacitive contributions due to double-layer charging). The top panels depict the Faradaic current traces (Figs. 3.1a and 3.1d), the m/z = 44 mass spectrometric ion current signals are shown in the central panels (Figs. 3.1b and 3.1e). Finally, the bottom panels depict the current efficiencies for CO₂ formation calculated from the above data (Figs. 3.1c and 3.1f). For more clarity, the forward-going scans and the negative-going scans are displayed in two separate panels, with the positive-
going scans in the left set of panels (Figs. 3.1a – 3.1c) and the negative-going scan in the right set of panels (Figs. 3.1d – 3.1f). Furthermore, the traces recorded at room temperature are also shown with higher magnification to better identify the shape (magnifications see figures). Furthermore, the onset behavior of the Faradaic and mass spectrometric currents is shown in insets with an expanded current scale.

The Faradaic currents at lower temperatures, up to 60°C, largely resemble those obtained in previous measurements, when accounting for the different reaction and transport conditions [10]. They were discussed in detail in ref. [10], therefore they will only be shortly summarized here. At potentials below about 0.35 V (23°C) (see inset), the electrooxidation of ethanol is essentially inhibited, which was explained by the presence of a reaction inhibiting (‘poisoning’) adlayer of adsorbed intermediates, mainly \( \text{CO}_{\text{ad}} \) and smaller amounts of adsorbed hydrocarbon residues (on a bare catalyst surface, at low \( \text{H}_{\text{upd}} \) and \( \text{CO}_{\text{ad}} \) coverages, ethanol was found to adsorb dissociatively, producing \( \text{CO}_{\text{ad}} \) and \( \text{CH}_{x,\text{ad}} \) species [10,41]). After the reaction onset, the current increases and passes through a broad peak, which consists of two hardly resolved states, a shoulder at \(-0.7\) V (at 23°C) and the peak maximum at 0.83 V (at 23°C, see magnified current trace).
Figure 3.1 Simultaneously recorded positive-going scan (a and b) and negative-going scan (d and e) of CVs (a and d) and MSCVs for m/z = 44 (b and d) and the corresponding CO₂ current efficiency (c and f) of the ethanol oxidation reaction on a Pt/Vulcan catalyst in 0.1 M ethanol solution pressurized with 3 bar Ar overpressure at elevated temperatures (temperatures see figure). Dashed lines: Magnified presentation of the room temperature traces (magnification factors see figure). Inset: Magnified presentation of the reaction onset. Arrows indicate the direction of the potential scan. Potential scan rate 10 mV s⁻¹, catalyst loading 40 µg_Pt cm⁻², electrolyte flow rate 15 µl s⁻¹.

By comparison with the ethanol adsorbate stripping behavior, the onset of the reaction is associated with the onset of ethanol adsorbate oxidation, which lowers the adsorbate coverage and allows increasing OH_ads formation and their reaction with EOR reaction intermediates [10]. At higher potentials (>0.83 V), the ethanol oxidation rate decreases, which is commonly assigned to an increasing OH_ads coverage/surface oxide formation on the Pt surface oxide formation [17], and reaches a plateau at 1.0 V. Even at potentials >1.0 V, ethanol oxidation continues at a low, but measurable rate up to the positive potential limit of 1.16 V. In order to
avoid possible electrooxidation of the carbon support, the upper potential limit was set to below 1.2 V.

With increasing temperature, the onset potentials shift to slightly lower values, reaching ~0.3 V at 100°C. The low-potential shoulder visible at 0.7 V at 23°C also shifts to lower potentials (~0.6 V at 100°C) and increases in intensity relatively to the main peak, such that at 100°C it forms a broad peak together with the previous main maximum and can no longer be resolved any more. Its further presence will become evident, however, in the CO₂ current efficiency (see below). The main maximum of the peak, finally, shifts from 0.85 V at 23°C to 0.75 V at 100°C respectively, following the trends known from previous model studies up to 60°C [10]. The smooth current decrease at the high-potential side of the peak extends to increasingly more positive values, reaching up to the positive potential limit of 1.16 V at 100°C. The maximum Faradaic current for ethanol oxidation increases considerably, by a factor of ca. 14, in the temperature range from 23°C to 100°C. The down-shift of the onset potential and in particular of the peak maxima with increasing temperature is related to the thermal activation of the ethanol adsorbate oxidation process and of the OH\textsubscript{ad} formation process (see also ref. [29,42,43]). Similar shifts were observed also in earlier temperature dependent studies of methanol oxidation on Pt and PtRu alloy electrodes, and attributed to an increasing thermal activation of water splitting [34,44-46]. Finally, also the high-potential current at potentials positive of 1.0 V increases significantly with temperature.

The m/z = 44 ion current signals largely follow the Faradaic current signals after correcting for the time delay between Faradaic current measurement and mass spectrometric measurement (time constant of the flow cell, ~4 s). CO₂ formation starts at 0.4 V at room temperature in the positive-going scan (see inset). After passing through a maximum at 0.73 V (23°C), it decreases again and reaches the baseline at 1.0 V. Compared to the Faradaic current signal, the peak is less broad, and mainly consists of a single state, which coincides with the low-potential state in the Faradaic current [10,25]. In a previous study, it was demonstrated that this peak is at least partly due to oxidation of adsorbed species (‘ethanol adsorbate’), that had been formed at lower potentials in the preceding negative-going scan, mainly CO\textsubscript{ad} and CH\textsubscript{x,ad} [25,41]. At potentials positive of 1.0 V, the CO₂ formation rate drops to values below the detection limit (23°C), in contrast to the finite value of the Faradaic
current at the potentials positive of 1.0 V. Therefore, the Faradaic current detected at potentials positive of 1.0 V must be related to incomplete oxidation of ethanol (formation of acetaldehyde and acetic acid) and/or Pt surface oxidation. Acetaldehyde formation was in fact detected previously up to 60°C when using a porous membrane [10]. With increasing temperature, both the onset potential for CO$_2$ formation and the potential of the peak maximum shift to lower potential, reaching 0.3 and 0.63 V at 100°C, respectively.

The corresponding current efficiencies for CO$_2$ formation, which were calculated as described before in Chapter 2 (Experimental part), are plotted in Fig. 3.1c. (The calculations were cut off at potentials where the Faradaic current is \(<1\%\) of its maximum value, because of the large errors resulting from even small deviations in the current measurement, introduced, as they can be introduced, e.g., by the double layer charge correction.) The current efficiencies are dominated by an initial increase with increasing potential, a maximum in the range 0.57 – 0.67 V, and a subsequent decay, reaching very low values at 1.0 V. With increasing temperature, the CO$_2$ current efficiency increases steadily, reaching a value of \(\sim45\%\) at the maximum at 100°C. At temperatures of 60°C and below, the maximum CO$_2$ current efficiencies are below 5%. The potential of the maximum decreases with increasing temperature, from 0.6 V at 60°C to 0.52 V at 100°C.

Comparing it with the CO$_2$ ion current signal, the maximum of the CO$_2$ current efficiency shifts more and more towards the onset of the CO$_2$ ion current signal. This agrees with the interpretation that the CO$_2$ formed at the onset of the CO$_2$ peak results mainly from the oxidation of ethanol adsorbates formed at lower potentials and in the preceding negative-going scan (see above). At room temperature, ethanol adsorbate oxidation even dominates the overall CO$_2$ formation. With increasing temperature, thermal activation results in an earlier onset of this reaction (cf. also with the down-shift in the onset of CO$_{ad}$ oxidation with increasing temperature [43]). This leads to vacant surface sites already at rather low potentials, where C-C bond breaking is more facile [47-50], and allows further CO$_{ad}$ formation and oxidation to CO$_2$, until C-C bond breaking ceases. In parallel, the EOR proceeds increasingly via incomplete oxidation to C$_2$ molecules (acetaldehyde and acetic acid). This interpretation agrees fully with our above statement that the Faradaic current peak consists of two states, a low-potential state with a higher contribution from CO$_2$ formation and a high-potential state
where the formation of incompletely oxidized C₂ species prevails [41, 51]. It should be noted that due to the contributions from the oxidation of pre-formed ethanol adsorbates, which provides only 2 electrons per CO₂ molecule rather than the 6 electrons assumed in the calculation (complete oxidation of ethanol to CO₂), the real values of the CO₂ current efficiency are lower than the maximum values in Fig. 3.1c.

The results quantitatively confirm that the current efficiency for CO₂ formation depends strongly on the electrode potential, in agreement with previous findings of DEMS [10, 20] and FTIR spectroscopy [52, 53] measurements on ethanol oxidation. Furthermore, it is important for realistic fuel cell applications that the overpotential for complete oxidation of ethanol to CO₂ decreases with increasing temperatures.

The negative-going Faradaic current scans resemble the positive-going scans in their general appearance, but exhibit distinct differences in details (Fig. 3.1d). At high potentials, the Faradaic currents first decrease and pass through a distinct minimum at ~1.0 V before increasing again, in contrast to the steady decrease with potential in this range in the positive-going scans. Furthermore, the Faradaic current peaks exhibit distinct double-peak characteristics, at least at higher temperatures ≥60°C. At low temperatures, only a single peak is resolved, which is centered at ca. 0.62 V at room temperature. With increasing temperature, two states develop, at 100°C the corresponding current maxima are located at about 0.65 V and 0.75 V. With decreasing potential, the Faradaic current decreases and reaches the zero level at about 0.3 V (see inset). At the respective peak potentials the Faradaic current increases by a factor of 10 when going from room temperature to 100°C.

CO₂ formation is completely suppressed over the entire potential range at temperatures below 40°C (see the magnified current trace), in agreement with findings in a previous DEMS study at room temperature [10, 25]. This was explained by the absence of preformed CO_ads in the negative-going scan, in combination with an effective inhibition of C-C bond breaking at potentials sufficiently high for CO_ads oxidation. At temperatures above 40°C, CO₂ formation is also observed in the negative-going scan, and increases steadily with increasing temperature. Since CO_ads oxidation is fast under these conditions (>0.7 V), the increasing rate of CO₂ formation in the negative-going scan directly reflects the increasing activation of C–C bond breaking (and fast subsequent oxidation to CO₂) under these conditions. Independent of the
temperature (at $\geq 40^\circ$C), it starts at $\sim 0.9$ V, passes through a broad maximum at $\sim 0.57$ V, and then decreases again to reach the baseline at $\sim 0.2$ V.

The observation of CO$_2$ at potentials were Faradaic currents are not detected, between 0.2 and 0.3 V, results from the finite decay time of the CO$_2$ signal: Time–response measurements performed for potential step oxidation of formic acid showed that after stepping from 1.0 to 0.06 V it takes about 10 s to reduce the CO$_2$ signal to 10% of its initial intensity, and about 25 s to decrease to the baseline. Therefore, the decrease of the CO$_2$ formation rates during ethanol oxidation at potentials below the peak maximum is more rapid than indicated by the mass measured data. In general, similar effects occur also in the positive-going scan, but in this case the CO$_2$ current decay is slower, and therefore these distortions contribute less.

Finally, the current efficiency for CO$_2$ formation was calculated in the same way as described above. Again, we obtain a steady increase coming from high potentials, and distinct peaks at potentials between 0.45 V at room temperature and 0.4 V at 100°C. The related CO$_2$ current efficiencies in the maxima are between 2.7% at 40°C and $\sim 50\%$ at 100°C (CO$_2$ formation is below the detection limit at temperatures up to 40°C). In this case, distortions due to oxidation of pre-formed ethanol adsorbates, mainly CO$_{\text{ad}}$, can be ruled out since at the high potentials CO$_{\text{ad}}$ is rapidly oxidized once formed. However, at lower potentials, in the potential range of the rapidly decaying CO$_2$ ion current, the finite decay time of the CO$_2$ signal described above will result in too high values of the CO$_2$ current efficiency. Therefore, also for the negative-going scan the real maximum CO$_2$ current efficiencies will be significantly lower than those displayed in Fig. 3.1f. (In the positive-going scans such effects are negligible in the potential range of the maximum CO$_2$ current efficiency). The general tendencies of an increasing CO$_2$ current efficiency with temperature and a decreasing CO$_2$ current efficiency with increasing potential at potentials positive of the maximum will not be affected by these effects. The rapidly increasing CO$_2$ current efficiency in the potential range between 0.6 and 0.45 V reflects the increasing activity for C-C bond breaking at these potentials. This will be discussed and compared with previous findings in more detail in the next section 3.2, together with the steady-state ethanol oxidation data.

It is interesting to note that with increasing temperature the peaks in the positive-going and negative-going scan become more and more similar, both for the Faradaic current and the
CO₂ ion current. This can be understood from the rapidly increasing reaction rate for CO₂ formation, which reduces the influence of the ethanol adsorbate layer on the reaction behavior more and more. It is oxidatively removed at increasingly lower potentials (pre-formed adsorbate layer in the positive-going scan) or can still be removed at potentials where C-C bond breaking and C₁,ad fragment formation are active (negative-going scan). At room temperature, CO₂ formation in the positive-going scan is essentially fully due to oxidation of COₐd pre-formed at lower potentials in the preceding negative-going scan, and in the negative-going scan CO₂ formation is inhibited. With increasing temperature, the pre-formed COₐd can be oxidized at increasingly lower potential, allowing subsequent bulk oxidation to CO₂ via C-C bond breaking and subsequent oxidation of the resulting C₁,ad species in the positive-going scan, and this contributes increasingly more to the CO₂ formation charge in the CO₂ ion current peak. In the negative-going scan, C-C bond breaking can occur at potentials where subsequent oxidation of the resulting fragments is still possible, and the latter reaction extends to lower potentials, where C-C bond breaking is increasingly active, until the surface is saturated with adsorbed C₁,ad fragments again. Since at more positive potentials the C₁,ad coverage is zero, the CO₂ ion current peak fully reflects the rate for C-C bond breaking, except for low potentials, where the resulting C₁,ad species are accumulated.

In order to evaluate the influence of the ethanol concentration on the activity and on the current efficiencies for complete ethanol oxidation to CO₂, we performed a similar series of cyclic voltammetry DEMS measurements at lower ethanol concentration (0.01 M) on the same Pt/Vulcan catalyst.

The positive-going (Figs. 3.2a) and negative-going (Fig. 3.2d) scans of the cyclic voltammogram for ethanol oxidation in 0.01 M solution closely resemble those obtained in 0.1 M solution (Figs. 3.1a – 3.1f) in their general appearance.
Figure 3.2  Simultaneously recorded positive-going scan (a and b) and negative-going scan (d and e) of CVs (a and d) and MSCVs for m/z = 44 (b and d) and the corresponding CO$_2$ current efficiency (c and f) of the ethanol oxidation reaction on a Pt/Vulcan catalyst in 0.01 M ethanol solution pressurized with 3 bar Ar overpressure at elevated temperatures (temperatures see figure). Dashed lines: Magnified presentation of the room temperature traces (magnification factors see figure). Inset: Magnified presentation of the reaction onset. Arrows indicate the direction of the potential scan. Potential scan rate 10 mV s$^{-1}$, catalyst loading 40 $\mu$g Pt cm$^{-2}$, electrolyte flow rate 15 $\mu$l s$^{-1}$.

Main differences compared to the higher concentration are: (i) The Faradaic current peak at 100°C is about $1/5$ of that in 0.1 M solution in both scan directions, (ii) the onset potential for ethanol oxidation in the positive-going scan is shifted to higher potentials (see insets in Figs. 3.1a and 3.2a), (iii) the low-potential peak in the positive-going scan is more pronounced and centered at 0.67 (23°C) – 0.56 V (100°C). Also, the CO$_2$ formation curves (Figs. 3.2b and
3.2e) largely resemble those in 0.1 M solution. Different than expected, the absolute currents are of comparable order of magnitude as in 0.1 M solution. Together with the significantly lower Faradaic currents in this case, this points already at higher current efficiencies in 0.01 M ethanol solution than in 0.1 M solution. This is confirmed by the CO$_2$ current efficiency curves in Figs. 3.2c and 3.2f. The CO$_2$ formation exhibits a potential dependence which resembles that obtained during 0.1 M ethanol oxidation. The absolute values, however, are significantly higher than in the latter case, with maximum values between 4% at 23°C and 78% at 100°C in the positive-going scan, and between below 7% at 40°C and formally above 100% at 100°C in the negative-going scan (see later discussion).

These results for lower ethanol concentrations fit well to trends determined in a previous study, where we observed higher relative CO$_2$ yields, relative to the formation of incomplete oxidation products, for oxidation of 0.01 M ethanol solution compared to 0.1 M ethanol oxidation [10]. Because of the relatively higher contribution from the oxidation of pre-formed ethanol adsorbate in the positive-going scan – the ethanol adsorption rate will be lower for lower ethanol concentrations – and because of the steeper decrease of the CO$_2$ formation current at potentials cathodic of the maximum in the negative-going scan, the differences between the actual (lower) maximum CO$_2$ current efficiencies and the measured values will be more pronounced than for reaction in 0.1 M solution. The general trend of an increasing CO$_2$ current efficiency with decreasing ethanol concentration and otherwise similar reaction conditions, however, resembles the behavior observed under steady-state conditions, in the potentiostatic measurements (see next section), and can therefore be considered as correct.

### 3.2.2 Potentiostatic oxidation of ethanol on Pt/Vulcan catalyst

More direct information on the ethanol oxidation kinetics and on the effect of the reaction potential is obtained from potentiostatic experiments, where potential and time effects are not convoluted. These also allow us to quantitatively determine the current efficiency for complete ethanol oxidation to CO$_2$ under steady-state conditions, where the experimental problems encountered in the determination of the CO$_2$ current efficiency in potentiodynamic measurements are absent.
Similarly to the potentiodynamic measurements, we followed the Faradaic current transients (Fig. 3.3a) and the mass spectrometric ion current transients for CO$_2$ formation (Fig. 3.3b, m/z = 44) at constant electrode potentials and different reaction temperatures, and calculated the corresponding CO$_2$ current efficiencies from these data (Fig. 3.3c).

**Figure 3.3** Simultaneously recorded transients of the Faradaic current (a) and the CO$_2$ ion currents for m/z=44 (b), and the corresponding current efficiency for CO$_2$ formation (c) during potentiostatic oxidation of ethanol on a Pt/Vulcan catalyst in 0.1 M ethanol solution pressurized with 3 bar Ar overpressure at elevated temperatures (temperatures see figure). Catalyst loading 40 µgPt cm$^{-2}$, electrolyte flow rate 15 µl s$^{-1}$.

Prior to the constant potential measurements, the negative-going potential scan was stopped at 0.06 V, and held there for 5 minutes. Therefore, the catalysts are partly covered by
adsorbates at the beginning of the experiment, which is close to the situation expected at the lowest reaction potential (0.18 V). Subsequently, the potential was stepwise increased, first to 0.18 V, and then in increments of 0.1 V to higher potentials. Each potential was held for 5 min, except for the highest potential of 0.68 V, because of the onset of bubble formation. Finally, the potential was stepped back to 0.06 V, holding at this potential until the background signal of the m/z = 44 ion current was sufficiently stable for proper background drift correction.

At potentials of 0.28 V and below, the Faradaic current (Fig. 3.3a) and the mass spectrometric ion current (m/z = 44) (Fig. 3.3b) are below the detection limit, which is attributed to the reaction inhibiting effect of the stable adlayer present on the catalyst under these conditions. This result agrees well with our findings in the potentiodynamic measurements, where the onset of ethanol oxidation occurred at ~0.3 V at 100°C and slightly more positive at lower temperatures (~0.35 V at 23°C). Measurable Faradaic currents and mass spectrometric CO$_2$ signals were detected at 0.38 V at higher temperatures (≥90°C, see insets in Figs. 3.3a, 3.3b), and at 0.48 V at all temperatures. From 0.48 V to 0.58 V and from 0.58 to 0.68 V, the Faradaic current increased by factors of 4.5 and 3, respectively. At 0.48 V, the Faradaic ethanol oxidation current still increases after the potential step, reaching a stable value after ~100 s. At higher potentials, the new Faradaic current values were reached almost instantaneously after each potential step, and the current remained stable at the respective value. The mass spectrometric CO$_2$ signals also increased with potential, but the increase was less pronounced, and for 0.68 V, the CO$_2$ signal was almost similar to that obtained at 0.58 V. Furthermore, at both 0.58 and 0.68 V, the CO$_2$ signal passed through a pronounced initial maximum and then decayed with time to approach the steady-state value. Note that after 300 s this was not yet fully reached. The initial maximum in the CO$_2$ ion current signal arises from the fast oxidation of part of the CO adlayer present under steady-state conditions at the former potential to CO$_2$, while at later stages, CO$_2$ formation is limited to the steady-state CO$_{ad}$ formation rate. The fact that this initial maximum in the CO$_2$ formation rate is absent in the Faradaic current indicates that with time incomplete oxidation of ethanol increases (at constant potential), compensating for the drop in partial reaction current for CO$_2$ formation. This increase of the rate for incomplete oxidation product formation has to be significant,
considering the much lower electron yield (2-4 electrons compared to 12 electrons per ethanol molecule). At all potentials, both the Faradaic current and the mass spectrometric CO$_2$ signal increased with temperature, as expected (see section 3.2.3). Above 70°C, the CO$_2$ formation increased steeply, by factors of between 9 and 15 from 70 to 100°C, depending on the potential.

The current efficiencies for CO$_2$ formation calculated from these data as discussed in Chapter 2 are plotted in Fig. 3.3c and listed in Table 3.1.

They show a clear tendency to i) decrease with increasing potential and ii) increase with increasing temperature. At 0.38 V, values of 18 and 23% were calculated for temperatures of 90°C and 100°C, respectively. At 0.48 V, they increase from 4.6% at 23°C to 45% at 100°C, for 0.58 V and 0.68 V the corresponding ranges of the CO$_2$ current efficiencies are 3.2 – 25.7 (23 – 100°C) and 1.6 – 12.6% (23 – 100°C), respectively. The increasing probability for CO$_2$ formation at elevated temperatures, in particular at temperatures of 60°C and above, agrees well with the findings in the potentiodynamic measurements in section 3.2.1. It indicates an increasing activation for C–C bond breaking. Furthermore, this and the equally increasing Faradaic currents demonstrate that also the resulting adsorbed C$_1$ reaction intermediates are rapidly removed. Apparently, the oxidation of the C-OH group, which results in the reaction by-products acetaldehyde and acetic acid, is much less activated (lower increase with temperature) than C-C bond breaking and CO$_{ad}$/CH$_{x,ad}$ oxidation (for further discussion see section 3.2.3).

Comparing the steady-state CO$_2$ current efficiencies with those obtained in the potentiodynamic measurements (Figs. 3.1c, 3.1f), we find the steady-state values to be in between those in the positive-going and negative-going scans. For instance, at 0.58 V reaction potential, values of about 26% (positive-going scan, negative-going scan: 10%) and 32% (positive-going scan, negative-going scan: 13%) were determined at temperatures of 90 and 100°C. The corresponding steady-state values are 20.1 and 25.7%. As discussed in section 3.2.1, at this potential the potentiodynamic data in the negative-going scan should be more affected by systematic distortions arising from the experiment (decay time of the CO$_2$ signal) than those in the positive-going scan. They are furthermore affected by the convolution of potential effects and time effects, and we would expect a lower adsorbate coverage in the negative-
going scan than under steady-state conditions. For the positive-going scan, this should be opposite. The influence of the varying adsorbate coverage is illustrated also in the temporal evolution of the Faradaic and CO$_2$ ion current transients before reaching steady-state conditions.

Table 3.1  Steady-state current efficiency for CO$_2$ formation (in percent) during constant potential ethanol oxidation at different concentrations, potentials and temperatures.

<table>
<thead>
<tr>
<th>T / °C</th>
<th>0.1 M EtOH</th>
<th></th>
<th>0.01 M EtOH</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.48 V</td>
<td>0.58 V</td>
<td>0.68 V</td>
<td>0.48 V</td>
</tr>
<tr>
<td>23</td>
<td>4.6</td>
<td>3.2</td>
<td>1.6</td>
<td>5.1</td>
</tr>
<tr>
<td>40</td>
<td>5.8</td>
<td>4.6</td>
<td>2.3</td>
<td>7.3</td>
</tr>
<tr>
<td>50</td>
<td>7.8</td>
<td>6.2</td>
<td>2.5</td>
<td>13.8</td>
</tr>
<tr>
<td>60</td>
<td>9.8</td>
<td>8.0</td>
<td>2.9</td>
<td>26.8</td>
</tr>
<tr>
<td>70</td>
<td>14.8</td>
<td>10.3</td>
<td>3.9</td>
<td>46.3</td>
</tr>
<tr>
<td>80</td>
<td>25.7</td>
<td>13.5</td>
<td>6.2</td>
<td>62.1</td>
</tr>
<tr>
<td>90</td>
<td>36.5</td>
<td>20.1</td>
<td>9.1</td>
<td>75.1</td>
</tr>
<tr>
<td>100</td>
<td>45.0</td>
<td>25.7</td>
<td>12.6</td>
<td>86.9</td>
</tr>
</tbody>
</table>

Going to lower potentials, the differences between CO$_2$ current efficiencies determined under steady-state conditions in the potentiostatic measurements and those derived from potentiodynamic measurements become even more pronounced. For instance, values of 24% (positive-going scan, negative going scan: 31%) and 34% (positive-going scan, negative-going scan: 42%) were calculated at 0.48 V for 90 and 100°C in the potentiodynamic measurements, compared to 36.5% and 45% under steady-state conditions. At this potential, not only effects arising from the convolution of potential and time effects (different adlayer coverage and composition in the potentiodynamic measurements) play a role, but also effects arising from the oxidation of adsorbates pre-formed at lower coverages (positive-going scan).
and from distortions in the measured CO$_2$ ion currents (negative-going scan) as discussed before in section 3.2.1 contribute significantly.

These results essentially preclude the use of CO$_2$ current efficiency values calculated from potentiodynamic data for quantitative discussions, and limit them to qualitative estimates of the CO$_2$ current efficiency.

Similar to the potentiodynamic experiments in section 3.2.1, we also evaluated the influence of the ethanol concentration on the ethanol oxidation activity and on the selectivity for complete oxidation to CO$_2$ under steady-state conditions, and similar potentiostatic measurements were performed in 0.01 M ethanol solution (Fig. 3.4).

The resulting current-time profiles closely resemble those obtained in 0.1 M solution, with measurable ethanol oxidation currents and CO$_2$ signals at potentials of 0.48 V and above. Also in this case, the Faradaic current increases significantly when going to 0.58 and 0.68 V. For the latter potential, however, the increase is less pronounced than for 0.1 M ethanol solution. For the mass spectrometric CO$_2$ signals, the steady-state ion currents even decrease between 0.58 V and 0.68 V.

The resulting current efficiencies for CO$_2$ formation, however, are generally higher than those measured in 0.1 M solution, yielding values between 87% (100°C) and 5.1% (23°C) at 0.48 V (see Table 3.1). Increasing the potential to 0.58 V, the range of the CO$_2$ current efficiencies decreased to between 32% (100°C) and 3.7% (23°C), and also at 0.68 V they are considerably higher than those obtained in 0.1 M ethanol solution (see Table 3.1). The pronounced increase in CO$_2$ current efficiencies compared to 0.1 M ethanol solution clearly demonstrates that the CO$_2$ current efficiencies at a given temperature depend strongly on the ethanol concentration. The simultaneous influence of reaction temperature and ethanol concentration is illustrated in Fig. 3.5, where the CO$_2$ current efficiencies obtained at 60°C, 80°C and 100°C are plotted for both concentrations and at the three potentials 0.48, 0.58 and 0.68 V. At the same temperature, the CO$_2$ current efficiency increases by a factor of 1.5 at 0.48 V and 100°C upon decreasing the concentration from 0.1 to 0.01 M. On the other hand, increasing the temperature from 80°C to 100°C at the same concentration (0.01 M) and electrode potential (0.48 V), the CO$_2$ current efficiency increased by about a factor of 1.4 (for a more extensive discussion see following section).
The present observation of slowly increasing CO$_2$ current efficiencies at temperatures up to 60°C differs from our findings in an earlier DEIMS study on ethanol oxidation on the same Pt/C catalyst, where the CO$_2$ current efficiency was found to decrease with temperature [10].

**Figure 3.4** Simultaneously recorded current transients of the Faradaic current (a) and the CO$_2$ ion currents for m/z=44 (b), and the corresponding current efficiency for CO$_2$ formation (c) during potentiostatic oxidation of ethanol on a Pt/Vulcan catalyst in 0.01 M ethanol solution pressurized with 3 bar Ar overpressure at elevated temperatures (temperatures see figure). Catalyst loading 40 µgPt cm$^{-2}$, electrolyte flow rate 15 µl s$^{-1}$.
Figure 3.5  Dependence of the steady-state current efficiency for CO\textsubscript{2} formation (potentiostatic measurements) on the variation of concentration at elevated temperatures and different potentials (see figure): 60°C (triangles), 90°C (circles) and 100°C (rectangles).

A similar discrepancy appears also between a previous DEMS study on methanol oxidation [54] and recent high-temperature/high-pressure measurements in our laboratory [38,55]. We explain this discrepancy in trends – in both EOR studies the absolute values of the CO\textsubscript{2} current efficiencies are low in this temperature range - by modifications of the CO\textsubscript{2} permeation behavior through the porous membrane used in these lower temperature DEMS studies [10,54], which reduce the CO\textsubscript{2} transport in the presence of methanol or ethanol compared to the calibration measurements, where these species are not present. Such effects are absent in the non-porous membrane used in the high-temperature/high-pressure measurements. These experimental effects will be corroborated and discussed in more detail in a forthcoming publication.

Similar observations of an increasing CO\textsubscript{2} current efficiency with higher temperatures were reported also for ethanol oxidation on a Pt or PtRu catalyst MEA in a DEFC by Aricó et
al. [19] and by Rao et al. [20]. The former authors reported a high CO$_2$ current efficiency of 95% for measurements in a DEFC (PtRu anode catalyst) at 145°C [19]. In the latter work, CO$_2$ current efficiencies of up to 75% were obtained at 0.6 V and 90°C in 0.1 M ethanol solution on a Pt/C catalyst MEA (slightly lower values at 0.5 and 0.7 V). Interestingly, very low values <5% were given, for PtRu catalysts. Furthermore, the CO$_2$ formation current efficiency was found to increase with catalyst loading, to decrease with increasing flow rate and also with ethanol concentration [20]. From the product yields reported by Rousseau et al. [6], who investigated ethanol oxidation in a 2M ethanol operated DEFC with a Pt/C anode, one can calculate CO$_2$ current efficiencies of 35% for reaction at 80°C (60% Pt/C catalyst, cell voltage 0.3 V equivalent to an anode potential voltage of ~0.55 V), which agrees qualitatively with the results by Rao et al., considering the much higher ethanol concentration.

In contrast, Wang et al determined acetaldehyde as main reaction product for reaction at 190°C in a DEFC operated by a highly concentrated ethanol solution (76% for an ethanol : water ratio of 1 : 2), with increasing water content the amount of CO$_2$ increased [9]. Higher CO$_2$ current efficiencies for decreasing ethanol concentrations were obtained also in model studies on ethanol oxidation over massive Pt electrodes [21,53] and over Pt/C catalyst thin-film electrodes [10].

The experimental findings in the above studies and in the present work can be summarized in the following correlations:

The current efficiency for CO$_2$ formation increases with

- increasing catalyst loading [10,20],
- decreasing electrolyte flow rate (decreasing mass transport) [20],
- decreasing ethanol concentration [10,20,21,53],
- decreasing electrode potential [20,21],
- higher reaction temperature [19,20].

The first three findings can be explained by transport effects, which are well known in Heterogeneous Catalysis, where in reactions with different products a lower space velocity is known to drive the product distribution towards their equilibrium composition [56]. In a microscopic picture, the increasing catalyst loading / decreasing electrolyte flow / decreasing
ethanol concentration increase the probability that volatile incomplete oxidation products, in the present case mainly acetaldehyde, can re-adsorb and react further to CO\textsubscript{2} before leaving the catalyst bed (‘desorption – re-adsorption – further reaction’ concept), as described in detail in ref. [57], and proposed already earlier for methanol oxidation [58]. These ‘re-adsorption – further reaction’ effects in fact become dominant under integral reaction conditions in a realistic fuel cell.

Specifically for ethanol oxidation, another effect may lead to decreasing CO\textsubscript{2} current efficiencies at higher ethanol concentrations. Reaction between acetaldehyde and ethanol may result in ethanal diethylacetal formation, which indeed was detected in the exhaust of a DEFC operated with pure ethanol [9]. This way, further reaction of acetaldehyde to CO\textsubscript{2} is inhibited, and the CO\textsubscript{2} current efficiency is reduced accordingly. With decreasing ethanol concentration (higher water-to-ethanol ratio), the yields of ethanal diethylacetal were found to decrease in that study, due to hydrolysis of ethanal diethylacetal to the initial reactants ethanol and acetaldehyde, and thus in an increasing CO\textsubscript{2} yield [9].

Furthermore, in dilute aqueous solutions, acetaldehyde is hydrated to the corresponding gem-diol [59,60], which in turn may decompose to CO\textsubscript{2} upon adsorption. Since in this case there is no additional oxygen required for CO\textsubscript{2} formation, this can lead to CO\textsubscript{2} formation even at low potentials, where water splitting is inhibited [61]. Similar effects were observed and discussed also for the adsorption / oxidation of formaldehyde [62-64]. Since acetaldehyde is formed as one of the two incomplete oxidation products during ethanol oxidation, its decomposition to CO\textsubscript{2} will also affect the CO\textsubscript{2} current efficiency and allow CO\textsubscript{2} formation even at potentials where water splitting and hence OH\textsubscript{ad} formation are essentially inhibited [65].

While there is no doubt about the general occurrence of these latter processes, a quantitative assessment of their contributions under present reaction conditions is not yet possible and will require further work, focusing on the adsorption / reaction behavior of acetaldehyde. The separation of contributions arising from these processes from general transport effects as described above (‘desorption – re-adsorption – further reaction’ concept) is complicated also since they result in a similar trend, namely an increasing CO\textsubscript{2} current efficiency with decreasing ethanol concentration.
Further modifications of the CO\textsubscript{2} current efficiency measured in a fuel cell may arise from an inhomogeneous distribution of the potential (current) in a fuel cell MEA [66,67], which can result in different product distributions over the flow field, while at the exhaust only the average value is measured.

The decrease in CO\textsubscript{2} formation with increasing potential is generally attributed to the decreasing tendency for C-C bond breaking with higher potential [47-50] and to the increasing coverages of OH\textsubscript{ad} / surface oxide species at higher potentials, which reduces the number of pairs of vacant surface sites required for C-C bond breaking (see also the discussion in the next section).

Finally, the increasing CO\textsubscript{2} current efficiency with higher temperature, which reflects a more pronounced temperature dependence and hence a higher activation barrier for CO\textsubscript{2} formation than for the overall ethanol oxidation process, will be discussed in the next section.

### 3.2.3 Apparent activation energies

The temperature dependent steady-state values of the Faradaic currents and the CO\textsubscript{2} ion currents (after normalization to a common $K^*_44$ value, see Chapter 2, Experimental part) were used to calculate the apparent activation energies $E_a$ for the overall oxidation of ethanol (Faradaic current) and for the complete oxidation of ethanol to CO\textsubscript{2} over the Pt/Vulcan catalyst at different reaction potentials.

As evident from the Arrhenius plots in Fig. 3.6, the logarithmic oxidation rates decrease linearly with 1/T, indicating that there is no change in the rate determining step in the entire temperature range covered (23 – 100 °C). From the slopes of the Arrhenius plots, we calculate activation energies of 42±2, 41±2, and 40±2 kJ mol\textsuperscript{-1} at potentials of 0.48, 0.58 and 0.68 V, respectively, for the overall ethanol oxidation reaction in 0.1 M ethanol solution. The corresponding activation energies for complete oxidation to CO\textsubscript{2} are 68±2, 67±2, and 65±3 kJ mol\textsuperscript{-1}, respectively (see Table 3.2). The apparent activation energy for the lower ethanol concentration (0.01 M) are 48±3, 46±3, and 41±2 kJ mol\textsuperscript{-1} for the overall ethanol oxidation reaction and 74±3, 73±1, and 69±3 kJ mol\textsuperscript{-1} for complete oxidation to CO\textsubscript{2}. 
Figure 3.6 Arrhenius plots of the overall ethanol oxidation rate (Faradaic current) and of the complete oxidation of ethanol to CO$_2$ (partial current for CO$_2$ formation) in 0.1 M ethanol solution (Fig. 3.6a) and 0.01 M ethanol solution (Fig. 3.6b) at different potentials (for potentials see figure). Electrolyte flow rate: 15 µl s$^{-1}$; catalyst loading 40 µg cm$^{-2}$.

Table 3.2 Apparent activation energies for the overall ethanol oxidation reaction (Faradaic current) and complete oxidation to CO$_2$ (CO$_2$ partial reaction current) at different ethanol concentrations and potentials, determined from steady-state reaction currents (see Fig. 3.6).

<table>
<thead>
<tr>
<th>E / V</th>
<th>0.1 M Ethanol</th>
<th>0.01 M Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ / kJ mol$^{-1}$</td>
<td>$E_a$(CO$_2$) / kJ mol$^{-1}$</td>
</tr>
<tr>
<td>0.48</td>
<td>42±2</td>
<td>68±2</td>
</tr>
<tr>
<td>0.58</td>
<td>41±2</td>
<td>67±2</td>
</tr>
<tr>
<td>0.68</td>
<td>40±2</td>
<td>65±3</td>
</tr>
</tbody>
</table>

The similarity of the corresponding apparent activation energies for 0.1 and 0.01 M ethanol solution and for the different potentials as well as the fact that the logarithmic rates lie on a straight line over the entire temperature range in the Arrhenius plots indicate that i) the apparent activation barriers measured in the two reaction pathways, respectively, can be
associated with a single reaction step, at least for complete oxidation to \( \text{CO}_2 \) (see also below), and that ii) the rate limiting steps are the same over the entire temperature and ethanol concentration range covered in the present study, but change with potential.

Our values of the apparent activation energy are significantly higher than those determined in previous fuel cell studies. Colmati et al. reported values of around 26 kJ mol\(^{-1}\) for the apparent activation energy, determined from the (steady-state) Faradaic current in a 1 M ethanol feed operated DEFC over a commercial Pt/C catalyst (20 wt.%) anode in the temperature range 70 to 100°C (cell potential 0.3 and 0.4 V, equivalent to an anode potential of 0.45 and 0.55 V, respectively) [68]. For PtRu/C catalysts, the corresponding value was ~32 kJ mol\(^{-1}\) in the same potential regime. Rao et al. obtained values of 31 kJ mol\(^{-1}\) for the overall reaction and 53 kJ mol\(^{-1}\) for complete oxidation to \( \text{CO}_2 \) at 0.6 V in measurements on a Pt/C catalyst MEA with a 40% Pt/C catalyst (0.1 M ethanol, temperature range 30-90°C) [20]. The activation energy for complete oxidation to \( \text{CO}_2 \) was calculated using mass spectrometric data after correcting the m/z = 22 (\( \text{CO}_2^{2+} \)) ion current for temperature effects. Comparison with the results of a previous model study [10], which covered reaction temperatures up to 60°C, is hardly possible, since in that study the activation energies were determined from potentiodynamic data, which as discussed above may result in considerable deviations from the steady-state situation.

The trend of a decreasing apparent activation barrier for the overall ethanol oxidation reaction upon going to higher ethanol concentrations, from 32 kJ Mol\(^{-1}\) in 0.1 M ethanol solution [20] to 26 kJ mol\(^{-1}\) in 1 M ethanol feed [68], agrees with the findings in our study, where the value decreased from 46±3 to 41±2 kJ mol\(^{-1}\) for changing from 0.01 to 0.1 M ethanol solution, and accordingly we expect the apparent activation energy to further decrease when going to even higher concentrations (1 M). The absolute values for the activation energies for the overall ethanol oxidation reaction, however, are significantly lower in the above studies than the values measured under comparable temperature and at similar potential in the present work (41±2 kJ mol\(^{-1}\) at 0.58 V in 0.1 M ethanol solution). Main reasons for this discrepancy are i) that the ethanol oxidation reaction proceeds via a complex network of individual reactions, where the Faradaic current only probes the sum of all partial reaction currents, and ii) the different mass transport conditions in model studies and in a real fuel cell.
Differences in the contributions from the various reaction pathways, which are likely to have different activation energies, will result in varying values of the apparent activation energy. The existence of some differences in the contributions from different pathways is illustrated by the still higher CO$_2$ current efficiencies obtained in the fuel cell measurements at similar temperature and anode potential (see discussion in the previous section) compared to our results. In summary, although we can not quantitatively explain the differences between the apparent activation energies for the ethanol oxidation reaction measured in fuel cell studies and in our model study at similar potential and temperatures, they can be understood on a qualitative basis.

The higher value of the apparent activation energy for complete oxidation of ethanol to CO$_2$ compared to the overall oxidation reaction is mainly attributed to a higher barrier for C-C bond breaking compared to oxidation of the C-OH group. This reaction step is not required for partial oxidation of ethanol to acetaldehyde and acetic acid, which at lower temperatures dominates the overall ethanol oxidation reaction and which only includes C-OH oxidation and water splitting (OH$_{ad}$ formation) as activated steps. Considering that with increasing temperature the complete oxidation to CO$_2$ contributes increasingly more to the overall reaction and that the effects on the ethanol oxidation current are even higher due to the higher number of electrons released during complete oxidation to CO$_2$ (12 electrons per ethanol molecule) than during partial oxidation to acetaldehyde (2 electrons per ethanol molecule) or to acetic acid (4 electrons per ethanol molecule), the barrier for the rate limiting step in the oxidation of the C-OH group must be even lower than the measured barrier of the overall ethanol oxidation reaction. Effects caused by the temperature dependent surface blocking by strongly adsorbed reaction intermediates / side products, mainly by CO$_{ad}$, should at least to zeroth order affect both reaction pathways, incomplete oxidation to acetaldehyde/acetic acid and complete oxidation to CO$_2$, in the same way. In a more detailed perspective, different site requirements may result in different site blocking effects for the two different pathways, which may result in slightly different effects for the two pathways.

In order to further elucidate the influence of C-C bond breaking, one may compare the present results with previous data on methanol oxidation. Wakabayashi et al. determined activation energies between 15 and 24 kJ mol$^{-1}$ in potentiodynamic measurements in a thin-
layer flow cell for potentials between 0.6 V and 0.7 V on a Pt electrode (temperature range 20°C – 120°C) [29]. On the other hand, Madden et al. reported activation energies of around 70 kJ mol⁻¹ at 0.35 V in a flow cell in potentiostatic measurements [30], and recent high-temperature DEMS measurements in our laboratory performed on the same catalyst and at the same experimental conditions as used in the present study led to activation energies of 58±3 kJ mol⁻¹, and 64±3 kJ mol⁻¹ for the overall methanol oxidation reaction and for complete methanol oxidation to CO₂, respectively, at 0.6 V (potentiostatic measurements) [55]. The differences between these values are mainly attributed to differences between potentiodynamic [29] and potentiostatic [30,55] measurements under steady-state conditions, additional effects arise from the differences in potential, electrolyte flow and electrolyte concentration. The rather similar values for the activation energies for complete oxidation to CO₂ of methanol and ethanol (67±2 kJ mol⁻¹) under these conditions may indicate that in both cases the same reaction step, e.g., CO_ad oxidation is rate limiting for this process. At higher potentials, CO₂ formation from ethanol will be limited by C-C bond breaking [47-50]. This interpretation is supported also by results of a recent HT / Hp DEMS study on the electrooxidation of ethylene glycole over the same Pt/C catalyst, where similar trends were observed as in the present study [69].

C-C bond breaking has two effects: it provides C₁,ad species which are required for the further oxidation to CO₂ (positive effect on the reaction), but the same species may block also the surface for further reaction (negative effect on the reaction). Only if the removal of these species is not rate limiting, a further increase of the C-C bond breaking rate will lead to an overall improvement of the reaction kinetics, i.e., a higher ethanol oxidation current. Otherwise, the increasing steady-state coverage of CO_ad and CH₅,ad species may result in a decrease of the ethanol oxidation current due to a decreasing partial oxidation of ethanol. For very low rates of CO_ad oxidation, also slow formation of these species is required to keep the steady-state coverage of these species at a level which still allows partial oxidation of ethanol (enough vacant surface sites for reaction). In that sense, catalysts with an improved activity for C-C bond breaking are not beneficial for the ethanol oxidation reaction, unless they are also more active for oxidation of adsorbed CO_ad and CH₅,ad species.
For technical applications finally it is important to note that increasing reaction temperatures not only result in a higher reaction rate, but, due to the higher activation barrier for complete oxidation of ethanol to CO$_2$ compared to its partial oxidation, also in decreasing amounts of acetaldehyde and acetic acid formation. Extrapolating the data in Fig. 3.6 to higher temperatures, one can estimate that under current reaction conditions and at 0.48 V complete conversion to CO$_2$ will be reached at ~140°C (0.1 M solution), provided there is no change in the reaction mechanism and rate determining pathways. For higher potentials, this temperature will shift to higher values (175°C at 0.58 V).

3.3 Conclusions

Potentiodynamic and potentiostatic DEMS measurements of the ethanol oxidation reaction on carbon supported Pt/Vulcan thin-film catalyst electrodes performed under fuel cell relevant but nevertheless well defined reaction and transport conditions (controlled electrolyte transport, continuous reaction, elevated temperatures and pressure) and on relevant materials (supported catalysts, 100% catalyst utilization), led to the following conclusions:

1. Both the overall reaction rate, as measured by the Faradaic current, and the rate for CO$_2$ formation increase significantly with increasing reaction temperature. The increase with temperature is much more pronounced for complete oxidation to CO$_2$ than for the overall ethanol oxidation reaction. Accordingly, the apparent activation energies are significantly higher for CO$_2$ formation than for the overall reaction (68±2 kJ mol$^{-1}$ vs. 42±2 kJ mol$^{-1}$ in 0.1 M ethanol solution, 0.48 V).

2. In the same way, also the current efficiency for CO$_2$ formation increases significantly with temperature, in particular at temperatures >60°C, from negligible CO$_2$ formation at room temperature under (4.6%, steady state conditions, 0.48 V) to 45% at 100°C. Accordingly, the formation of incomplete oxidation products (C$_2$ by-products), which is dominant at ambient temperature, decreases significantly with temperature. High current efficiency values for CO$_2$ formation over the Pt/C catalyst can be reached, however, only at low potentials (0.38 and 0.48 V) and hence at rather low current densities (geometric surface area normalized current density): 23% at 0.4 mA cm$^{-2}$ (0.38 V, 0.1 M ethanol solution), 45% at 3.7 mA cm$^{-2}$ (0.48 V,
at 0.1 M ethanol solution), and 87% at 2.3 mA cm\(^{-2}\) (0.48 V, 0.01 M ethanol solution) (all at 100°C).

3. The activation energies decrease slightly with potential, from 48±2 and 68±2 kJ mol\(^{-1}\) at 0.48 V to 40±2 and 65±3 kJ mol\(^{-1}\) at 0.68 V in 0.1 M solution for the overall reaction and the pathway for CO\(_2\) formation, respectively. Correspondingly, also the current efficiencies for CO\(_2\) formation decrease with increasing potential, e.g., from 45% (14.8%) at 0.48 V to 12.6% (3.9%) at 0.68 V at 100°C (70°C). The decrease in both quantities with potential is associated with the transition from rate limiting CO\(_{ad}\) oxidation at lower potentials to rate limiting C-C bond breaking (CO\(_{ad}\) formation) at higher potential (see point 2).

4. The current efficiency for CO\(_2\) formation increases with decreasing ethanol concentration, e.g., from 48% in 0.1 M to 87% in 0.01 M ethanol solution (0.48 V, 100°C). This increase in CO\(_2\) formation is explained by transport effects, namely an increasing tendency for re-adsorption and further oxidation of incomplete oxidation products at lower concentrations. Similar effects are proposed also as origin for the increasing CO\(_2\) current efficiency with increasing catalyst loading and decreasing electrolyte flow reported in the literature.

5. Significant differences between the CO\(_2\) current efficiencies determined in potentiodynamic measurements and under steady-state conditions in potentiostatic measurements at similar potentials are explained by a combination of different effects specific for potentiodynamic measurements: (i) the convolution of potential and time effects in potentiodynamic measurements, which result in different adlayer coverages and compositions in both types of measurements; (ii) the oxidation of adsorbed species pre-formed at other (lower) potentials, which leads to lower electron yields per CO\(_2\) molecule formation, and (iii) distortions in the CO\(_2\) detection induced by the experiment. Due to these effects, only the CO\(_2\) current efficiencies determined under steady-state conditions are reliable for quantitative considerations, while the use of values determined in potentiodynamic measurements is limited to qualitative discussions of the trends.

6. The increasing similarity between the signals in the positive-going and negative-going scans in potentiodynamic measurements with higher temperatures is attributed to increasing contributions from ethanol bulk oxidation (decreasing contributions from pre-formed adlayer
oxidation) due to the rapidly increasing activity. Hence, with increasing temperatures the system increasingly approaches steady-state conditions during potentiodynamic measurements.

7. The effective overall reaction rates and the CO$_2$ formation rates measured between 60°C and 100°C in the present study quantitatively follow the trends determined in the lower temperature range between room temperature and 60°C in this and earlier studies, as illustrated by the linear correlation between ln i and 1/T over the full temperature range in the Arrhenius plots. Therefore we conclude that the rate limiting reaction steps in the two reaction pathways do not change in the entire temperature scale. Extrapolating these data to higher temperatures leads to complete ethanol conversion to CO$_2$ in 0.1 M ethanol solution (100% CO$_2$ current efficiency) at ~140°C under present reaction conditions (0.48 V).

Finally, the drastic temperature and concentration effects evident from the present study demonstrate the importance of fuel cell relevant reaction and mass transport conditions (continuous reaction, continuous electrolyte and elevated temperature/pressure) in model studies aiming at a proper description of the reaction kinetics and the reaction mechanism in a realistic fuel cell.

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3.5 References


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Chapter 4

Electrooxidation of acetaldehyde on a carbon supported Pt catalyst at elevated temperature/pressure: An on-line differential electrochemical mass spectrometry study
The content of the following section is extracted from an article by S. Sun, M. Heinen, Z. Jusys, and R.J. Behm, “Electrooxidation of acetaldehyde on a carbon supported Pt catalyst at elevated temperature/pressure: An on-line differential electrochemical mass spectrometry study”, which has already been published in the Journal of Power Sources, 204, 1-13, 2012. It is adopted with permission from Elsevier, © 2012. The corresponding figures and tables have been adapted to fit the layout of the thesis. The experimental description for the following section is represented in Chapter 2. The figures, tables and the corresponding descriptions shown in the following section are same as published. The majority of the data acquisitions, evaluation, graphing and writing of the manuscript were done by the author of this thesis.

Abstract

The electrooxidation of acetaldehyde on a Pt/Vulcan catalyst was investigated over a wide range of temperatures (23 – 100°C) in a flow cell under controlled transport conditions, employing high temperature / high pressure (3 bar overpressure) on-line differential electrochemical mass spectrometry (DEMS). Potentiodynamic and potentiostatic measurements of the Faradaic current and of the CO₂ formation rate reveal that complete oxidation to CO₂ prevails only at higher temperatures and lower potentials, with ~80%/40% current efficiency for CO₂ formation at 0.5 V/0.6 V in 0.1 M solution and at 100°C, in contrast to a few percent at room temperature. Oxidation to acetic acid increases at higher potential. The increase of the CO₂ current efficiency with temperature is reflected by a higher apparent activation barrier for complete oxidation to CO₂ (39±2 kJ mol⁻¹ at 0.6 V, 0.1 M) compared to that of the overall acetaldehyde oxidation reaction given by the Faradaic current (32±2 kJ mol⁻¹) and that for oxidation to acetic acid (27±3 kJ mol⁻¹). Analogous measurements on the electrooxidation of acetic acid show very low reactivities even at 100°C, and a high apparent activation energy (173±6 kJ mol⁻¹). The importance of fuel cell relevant reaction and mass transport conditions in model studies is discussed.
4.1 Introduction

Since acetaldehyde and acetic acid are reaction side products and possibly also reaction intermediates of the ethanol oxidation reaction [1-6], their interaction with metal electrode surfaces and supported catalysts is highly relevant for understanding the reaction characteristics in direct ethanol fuel cells (DEFCs) [7-12]. Accordingly, these reactions have been studied on a number of electrodes and supported catalysts [1,5,6,13-20]. Different from reaction conditions in a fuel cell, however, most of these studies were performed under ill-defined transport conditions and at room temperature. Recently, we reported on the reaction characteristics of the ethanol oxidation reaction (EOR) over a carbon supported Pt/C fuel cell catalyst, which was studied under enforced and controlled electrolyte flow over a wide range of temperatures (23 – 100°C) in a model study performed on a thin-film Pt/C catalyst electrode [21]. This study revealed drastic effects of the reaction temperature on the reaction characteristics. In particular, the selectivity for CO$_2$ formation was shown to increase to 45% (at 0.48 V, in 0.1 M acetaldehyde solution) for reaction at 100°C, and temperatures of ~140°C were estimated for reaching complete conversion to CO$_2$ [21]. For a further improved understanding of the reaction behavior in the DEFC, it would be highly desirable to also know the reaction behavior of the incomplete EOR products acetaldehyde and acetic acid under relevant, but nevertheless well-defined reaction and transport conditions at elevated temperatures. This is a topic of the present paper, where we report results of a high temperature / high pressure differential electrochemical mass spectrometry (HT / Hp-DEMS) study in the same temperature range (23 – 100°C).

Before going into details, we will briefly summarize the main findings on the adsorption and electrooxidation of acetaldehyde and acetic acid reported in previous studies [1,3,4, 6,14,17,19,20,22-28]. Studying the acetaldehyde oxidation reaction (AOR) at a polycrystalline Pt electrode in acidic solution by in situ SNIFTIR spectroscopy, Rasch and Iwasita found that the main reaction products are CO$_2$ and acetic acid, with the product yield depending sensitively on the acetaldehyde concentration [23]. For the lowest acetaldehyde concentration (0.01 M), CO$_2$ was detected as the only reaction product, while for higher acetaldehyde concentrations (0.1 M and 1 M), both CO$_2$ and acetic acid were identified at comparable selectivities. The authors proposed that the pathway leading to CO$_2$ formation (in
potential scans) is limited by the coverage of adsorbate species formed at low potentials. Rodríguez et al. [3] investigated the adsorption and oxidation of acetaldehyde on single-crystalline Pt(111) and Pt(100) electrodes by in situ FTIR spectroscopy, reporting CO_{ad} and adsorbed acetaldehyde/ acetyl species formation. They suggested that CO$_2$ is produced via oxidation of strongly adsorbed intermediates, CO$_{ad}$ and adsorbed acetaldehyde/acetyl species, but that none of these adsorbates is the intermediate in the pathway leading to acetic acid. Recently, Farias et al. [6] reported a systematic in situ FTIR spectroscopy study correlating the yields of CO$_2$ and acetic acid at polycrystalline Pt with the acetaldehyde concentration. They proposed that at high concentration (0.5 M), acetaldehyde molecules and water molecules compete for active sites, which increasingly hinders the oxidation of adsorbed species and thus the pathway to CO$_2$ formation. Adsorbed acetaldehyde/acetyl species were proposed to act as the decisive intermediate, which is responsible for the reaction branching to either dissociation at medium potentials (< 0.5 V) or to oxidation to acetic acid (> 0.7 V) [19]. These intermediate species were identified recently using surface enhanced FTIR spectroscopy in an Attenuated Total Reflection (ATR) configuration [20,26,27]. Dissociative adsorption of acetaldehyde was recently confirmed to result in both CO$_{ad}$ and CH$_x$ species using in situ surface enhanced Raman spectroscopy [28] and ATR-FTIRS [20]. Adsorption and oxidation of acetaldehyde on carbon supported Pt/C catalysts [17,25] and on porous Pt and Rh electrodes [4,14] was also studied by DEMS. These studies revealed the formation of CO$_{ad}$ and adsorbed hydrocarbon residues, where the latter species can be oxidized at potentials higher than 1.0 V or reductively desorbed as hydrocarbons upon hydrogen adsorption at low potentials. Based on the literature results, it is generally assumed that on Pt group metals acetaldehyde oxidation to CO$_2$ proceeds via oxidation of adsorbed species formed upon dissociative adsorption of acetaldehyde, with the total CO$_2$ product yield being in the range of a few percent at room temperature and at not too high potentials[17]. This was verified by a number of investigations on Pt/C [17,25] and PtRu/C or Pt$_3$Sn/C [17] catalyst electrodes, well-defined platinum single-crystal electrodes (Pt(111), Pt(100)) [3,19], on Pt thin film electrodes [20,26,28], and on Rh electrodes [4,14] (and references therein). At higher potentials, dissociative adsorption is increasingly hindered. At potentials >1.0 V, it is essentially inhibited due to surface blocking by adsorbed oxy-species, which was concluded
by comparison with previous FTIR results [6,20,26,28,29]. Under these conditions, oxidation of the formyl group to carboxyl leads to acetic acid formation.

Acetic acid adsorption/oxidation was also mainly studied at ambient temperatures on Pt electrodes [1,2,20,31]. Electrochemical, radiotracer and FTIR spectroscopy studies of the acetic acid adsorption behavior over polycrystalline and single crystalline platinum electrodes revealed a reversible adsorption of acetate anions in a twofold coordinated configuration, via the two oxygen atoms of the carboxyl group (see, e.g., [1,2,20,22,24,26]). The activity for C-C bond dissociation and further oxidation was found to be negligible at ambient temperatures. Therefore, formation of acetic acid was often assumed to be a “dead-end” in ethanol oxidation [31]. Thermal activated acetic acid oxidation on Pt was reported only at rather high temperatures, e.g., at 200°C and above in an autoclave electrochemical cell [32].

Unfortunately, a direct transfer of these results to the reaction situation in a realistic fuel cell is hardly possible, since most of the model studies were performed at room temperature, while DEFC’s are operated at elevated temperatures [7-12,33,34]. On the other hand, detailed studies of the reaction characteristics, in particular its selectivity, performed using realistic fuel cells, are rare [31,35]. Rao et al. [31] investigated ethanol oxidation, acetaldehyde oxidation and acetic acid oxidation in an operating fuel cell environment over Pt/C, PtRu/C and Pt3Sn/C catalysts and showed that acetaldehyde is quite active for further oxidation, while acetic acid is resistant against further oxidation. Furthermore, a quantitative analysis of the product yields in a DEFC can be largely influenced by oxygen crossover from the cathode, resulting in additional oxidation of acetaldehyde to acetic acid, and/or losses of acetaldehyde due to crossover to the cathode side, both of which result in an apparent increase of the acetic acid yield at the anode [35]. In addition, the reaction conditions in a DEFC are generally much less defined than those in model studies, which may also lead to diverging results between different types of studies.

To bridge the gap between model studies and realistic fuel cell measurements, we recently developed a high-temperature/high-pressure DEMS set-up, which is based on an elevated temperature channel flow cell [36] interfaced to a mass spectrometer via a low-permeability Teflon membrane [37]. The set-up allows electrocatalytic measurements on supported catalyst thin-film electrodes (ca. 100% catalyst utilization, negligible diffusion limitations) at elevated
temperatures (up to 100°C) and pressure (3 bar overpressure) under continuous reaction and well-defined, enforced mass transport conditions. The complete oxidation product \( \text{CO}_2 \) can be determined quantitatively and it is thus possible to discriminate between partial and complete oxidation under realistic reaction conditions, which is particularly interesting for practical applications. Following previous studies of the electrooxidation behavior of small organic molecules such as ethanol [21], methanol [38], and ethylene glycol [39], this set-up was employed in the present work for a quantitative study of the activity/selectivity of the acetaldehyde oxidation reaction (AOR) and of the acetic oxidation reaction over a Pt/C catalyst at elevated temperatures and continuous reaction/mass transport conditions.

In the following part, we will present and discuss results of potentiodynamic (section 4.2.1) and potentiostatic (section 4.2.2) HT / Hp-DEMS measurements in 0.1 M, 0.01 M and 0.001 M acetaldehyde solutions. The electrooxidation of acetic acid at constant potentials and elevated temperatures will be topic of section 4.2.3. The apparent activation energies for the overall oxidation and for complete oxidation to \( \text{CO}_2 \) at different potentials, both for acetaldehyde and acetic acid molecules, will be derived and discussed in the last part (section 4.2.4). Finally, the mechanistic and kinetic implications arising from these data for realistic fuel cell operation will be discussed.

4.2 Results and discussion

4.2.1 Potentiodynamic oxidation of acetaldehyde

Fig. 1 shows potentiodynamic acetaldehyde oxidation traces recorded during continuous potential cycling (10 mV s\(^{-1}\) scan rate) in 0.5 M H\(_2\)SO\(_4\) solution containing 0.1 M acetaldehyde at different temperatures (23, 40, 60, 80 and 100°C). For more clarity, the cyclic voltammograms are presented as separate plots for the positive-going (Figs. 4.1a–4.1c) and negative-going scans (Figs. 4.1d–f). Faradaic current traces (Figs. 4.1a and d), mass spectrometric ion current signals at m/z = 44 (Figs. 4.1b and e) and current efficiencies for \( \text{CO}_2 \) formation (Figs. 4.1c and f) are depicted in the upper, middle and bottom panels, respectively. The values of current efficiencies were calculated only for potentials, where the corresponding Faradaic current is above 1% of its maximum value. In the insets, the Faradaic
and mass spectrometric currents are shown at higher magnification. Furthermore, the room temperature CVs traces are shown for comparison on a magnified scale in the main panels.

At 23°C, the general pattern of the Faradaic currents is similar to that reported previously under similar reaction and transport conditions over a Pt/C catalyst [17,25]. In the positive-going scan, the onset of acetaldehyde oxidation is largely suppressed at low potentials (<0.45 V, see inset), which is attributed to the presence of inhibiting adsorbed reaction intermediates, mainly CO$_{\text{ad}}$ and CH$_{x,\text{ad}}$ species formed during the negative-going scan via dissociative adsorption of acetaldehyde [6,25,28]. At potentials above 0.45 V, the reaction starts and the Faradaic current increases, passes over a shoulder at ~0.73 V and reaches its maximum value at ~0.9 V (23°C, see magnified current trace). The onset of the acetaldehyde oxidation corresponds to the onset of oxidation of acetaldehyde adsorbate (CO$_{\text{ad}}$ at these potentials) [25]. After having passed the maximum, the acetaldehyde oxidation current decreases at higher potentials, which was attributed to an increasing hindrance for acetaldehyde dissociation, e.g., by adsorbed oxy-species formed at these potentials[3,17,20]. At potentials above 1.0 V, the acetaldehyde oxidation rate increases again, in contrast to the behavior of the EOR [21,26,44].

Increasing the temperature, we observed the following characteristic changes in the positive-going scan: (i) the Faradaic current increases significantly, by more than an order of magnitude from 23°C (peak current 0.36 mA) to 100°C (peak current 3.9 mA); (ii) the onset potential shifts negatively, from 0.45 V at 23°C to ~0.42 V at 100°C; (iii) the position of shoulder, centered at 0.73 V at 23°C, also shifts negatively to about 0.6 V at 100°C; (iv) the potential of the peak maximum shifts from ~0.9 V at 23°C to 0.84 V at 100°C. The thermal activation of the reaction, which agrees with similar tendencies in the temperature dependent ethanol oxidation reaction [21], can result from an activation of the C-C dissociation step, activation of the OH$_{\text{ad}}$ formation, partial thermal desorption of the reaction inhibiting adsorbed intermediates [43], and/or activation of the reaction between the above reactants [44-51].

Comparing acetaldehyde oxidation with ethanol oxidation under identical reaction conditions [21], the peak current at 100°C for acetaldehyde electrooxidation is ~4.5 times lower than that for ethanol electrooxidation under otherwise similar conditions. This is in
agreement with the previous finding that the dissociative adsorption of acetaldehyde (C-C bond breaking) is more facile compared to ethanol adsorption, which was attributed to the higher polarity of the acetaldehyde molecule (aldehyde group vs. hydroxyl group) [25,28]. The resulting higher formation rate of adsorbed C1 species, which can irreversibly adsorb onto the electrode surface, results in a rapid poisoning of the surface at potentials where oxidation of these species is slow.

The corresponding Faradaic current patterns in the negative-going scans are shown in Fig. 4.1d. They differ distinctly from the positive-going scans in Fig. 4.1a. Starting from the anodic potential limit, the Faradaic currents first decrease, pass through a distinct minimum at ~0.9 V, then increase again after reduction of PtO, until reaching a current maximum at ~0.6 V via a shoulder located at ~0.75 V. Continuing the scan to more negative potentials, the Faradaic current decreases until it reaches the detection limit (at 100°C at ~0.4V, see inset in Fig. 4.1d). Upon increasing the temperature, the Faradaic current increases steadily, and at 100°C the maximum current value is ~8 times higher than at room temperature. The current profile develops with temperature from two resolved single peaks centered at 0.75 V and 0.6 V, respectively (both at 23°C), to a broad single peak at 100°C.
Chapter 4 Electrooxidation of acetaldehyde on a carbon supported Pt catalyst at elevated temperatures...

Figure 4.1 Simultaneously recorded positive-going scan (a and b) and negative-going scan (d and e) of CVs (a and d) and MSCVs for m/z = 44 (b and d) and the corresponding CO₂ current efficiency (c and f) of the acetaldehyde oxidation reaction on a Pt/Vulcan catalyst in 0.1 M acetaldehyde solution pressurized with 3 bar N₂ overpressure at elevated temperatures (temperatures see figure). Dashed lines: Magnified presentation of the room temperature traces (magnification factors see figure). Inset: magnified presentation of the reaction onset. Potential scan rate 10 mV s⁻¹, catalyst loading 40 µg cm⁻², electrolyte flow rate 15 µl s⁻¹.

The CO₂ formation rate at m/z = 44 (Fig. 4.1b), after correction of the time delay between formation and detection (~4 s in our case, details see chapter 2, experimental part), first follows the Faradaic current traces. At 23°C in the positive-going scan, the onset formation of CO₂ appears at around 0.5 V, followed by a steady increase of the ion current until reaching its maximum value at about 0.74 V. Then it decreases again to the background level, which is reached at 1.1 V. Hence, independent of the reaction temperature, CO₂ formation is inhibited at higher potentials. Accordingly, the increase of the Faradaic current at very positive potentials must be due to incomplete oxidation of acetaldehyde to acetic acid. These findings are in agreement with the spectroscopic detection of adsorbed acetate formation during...
acetaldehyde oxidation at potentials above 0.7 V, where the Pt surface is covered by significant amounts of OH$_{ad}$ species [3,6,19,20,23,52]. Comparison with the Faradaic current peak reveals that the ion current peak coincides with the shoulder at ~0.73 V (at 23°C) in the Faradaic current mentioned above (Fig. 4.1a). The low-potential shoulder was therefore ascribed to the complete oxidation of adsorbed species, which were formed at lower potentials, to CO$_2$ (mainly CO$_{ad}$ oxidation at these potentials) [6,17,25,28,53]. With increasing reaction temperature, the onset potential of the CO$_2$ formation peak shifts negatively to 0.4 V at 100°C, and the intensity in the ion current peak increases by one order of magnitude.

In the negative-going scan, CO$_2$ formation is completely suppressed over the entire potential range at ambient temperature (Fig. 4.1e). With increasing temperature (≥ 40°C), CO$_2$ formation sets in and increases at potentials below 0.9 V. It reaches its maximum values at about 0.7 V, and then decreases again to the background level, which is reached at about 0.2 V. It should be noted that in contrast to the positive-going scan, the catalyst surface is initially oxidized in the negative-going scan when coming from higher potentials, and therefore the formation of CO$_{ad}$ is hindered over a wide potential range [20,21,26]. In the positive-going scan, the temperature dependence of CO$_2$ formation reflects the temperature dependence of the oxidation of CO$_{ad}$ pre-formed at lower potential, whereas in the negative-going scan, C-C bond rupture starts at potential where the resulting fragments can also be oxidized (negligible C$_{1,ad}$ coverage), and the temperature dependence reflects the combined temperature dependence of Pt surface reduction and C-C bond breaking.

The resulting patterns of the current efficiency for CO$_2$ formation are shown in Figs. 4.1c and 4.1f. In the positive-going scan (Fig. 4.1c), it exhibits a distinct temperature and potential dependence. Since acetaldehyde oxidation results only in two reaction products and one of them (CO$_2$) is detected quantitatively, the current efficiency for acetic acid formation can simply be deduced from the difference between 100% and the current efficiency for CO$_2$ formation. The CO$_2$ current efficiency exhibits its maximum at potentials between 0.5 - 0.7 V for all temperatures, followed by a subsequent decay at higher potentials. Increasing the temperature, the CO$_2$ current efficiency increases as well, reaching maximum values of ~80% at 100°C (at ~0.57 V), while at 23°C the maximum value of about 20% is reached at 0.66 V.
As mentioned before, the Faradaic current at the onset of the current peak is largely attributed to the oxidation of acetaldehyde adsorbate, mainly CO$_{ad}$, which was formed at lower potentials and in the preceding negative-going scan. Since this results exclusively in CO$_2$ formation, it is not surprising that the maximum of the CO$_2$ current efficiency in the positive-going scan appears at the onset of the Faradaic current. Considering furthermore that the onset of pre-adsorbed CO$_{ad}$ oxidation also shifts to lower potentials with increasing temperature [48,49,54], the earlier onset of the Faradaic current is easily explained. It also indicates that the down-shift of the onset potential with increasing temperature will allow oxidation to CO$_2$ via C-C bond breaking after the oxidation of CO$_{ad}$ preformed at lower potentials, and also result in larger contribution to CO$_2$ formation than would be obtained in the absence of these preformed species. Hence, the earlier onset of the Faradaic current is partly or even largely an artifact of the potentiodynamic experiment, and would not be observed under potentiostatic reaction conditions (see 4.2.2). Similar observations were reported recently for ethanol oxidation under the same experimental conditions [21].

The decay of the CO$_2$ current efficiency at more positive potential indicates that at higher potentials the acetaldehyde oxidation reaction proceeds increasingly via an incomplete oxidation pathway (producing acetic acid). Finally, it is important to note that the apparent values obtained for the CO$_2$ current efficiency in the onset region of the Faradaic current in the positive-going scan are systematically too high: while the actual number of electrons required for oxidation of CO$_{ad}$ pre-formed by dissociative adsorption of acetaldehyde at lower potentials is two, the calculations of the CO$_2$ current efficiency (Eq. 1) assume five electrons per resulting CO$_2$ molecule when converting the mass spectrometric m/z=44 current into the partial current for acetaldehyde oxidation to CO$_2$. Therefore, the actual values of the CO$_2$ current efficiency for acetaldehyde oxidation are lower than those shown in Fig. 4.1c.

In the negative-going scan (Fig. 4.1f), the current efficiencies for CO$_2$ formation increase steadily with decreasing potential, but remain at rather low levels. The maximum values range from ca. 10% at 60°C to about 20% at 100°C (both at 0.5 V). Since the electrode surface is free from reaction inhibiting adsorbed species during the negative-going scan after the reductive removal of OH$_{ad}$/oxide surface species, the increase of the CO$_2$ current efficiency between 0.6 and 0.45 V initially reflects the increasing activation for C-C bond breaking, until at lower potentials the build-up of strongly adsorbed species sets in. The apparent increase in
the current efficiency for CO₂ formation at low potentials (below 0.4 V) in the negative-going scan results from an experimental artifact (for details see Ref. [21]), from the limited off-transport of the considerable amounts of CO₂ formed at the maximum reaction rates from the electrochemical cell to the membrane inlet. This leads to a longer delay of the mass spectrometric signal decay compared to the instantaneous decrease in the Faradaic current (see corresponding insets). Therefore, the current efficiency for CO₂ formation at lower potentials in the negative-going scan was not considered to be meaningful and thus not plotted.

In order to quantitatively determine the role of the acetaldehyde concentration on the activity and selectivity of the acetaldehyde oxidation reaction, we performed similar cyclic voltammetry DEMS measurements at lower acetaldehyde concentrations (0.01 and 0.001 M) under otherwise identical experimental conditions. The cyclic voltammograms for acetaldehyde oxidation in 0.01 M acetaldehyde solution (Figs. 4.2a–f) show an overall behavior rather similar to those obtained in 0.1 M solution, with an increased relative contribution of the lower potential peak in the Faradaic current in the positive-going scan, which becomes dominant at 0.01 M acetaldehyde concentration. For reaction in 0.001 M solution (Figs. 4.3a–f), the CVs exhibit distinct oxide reduction peaks in the potential range from 0.8 V to 0.9 V, overlapping with the acetaldehyde oxidation current in the negative-going scan.

A quantitative evaluation of the electrooxidation behavior for different acetaldehyde concentrations at 100°C shows:

i) The maximum currents in the Faradaic current peaks decrease with decreasing concentration. In 0.01 M acetaldehyde solution, they are about \( \frac{1}{3} \) (positive-going scan) and \( \frac{1}{2} \) (negative-going scan) of those in 0.1 M solution, and in 0.001 M acetaldehyde solution, they are about \( \frac{1}{8} \) (positive-going scan) and \( \frac{1}{15} \) (negative-going scan).
ii) The peak currents of the m/z = 44 ion signals also decrease with decreasing concentration, to about \( \frac{1}{2} \) (positive-going scan) and \( \frac{2}{5} \) (negative-going scan) of that in 0.1 M solution in 0.01 M acetaldehyde solution, and to about \( \frac{1}{3} \) (positive-going scan) and \( \frac{1}{8} \) (negative-going scan) in 0.001 M acetaldehyde solution.

iii) The onset potentials for acetaldehyde oxidation (both Faradaic current and m/z = 44 ion current signal) in the positive-going scan are shifted to lower potential with decreasing acetaldehyde concentration (see insets in the respective figures).
iv) The peaks become narrower for lower concentrations, together with a distinct transition from broad two-state peaks to single-state peaks and the potential of the peak maximum also shifts negatively. On the other hand, the tendency of the CO$_2$ current efficiency change with potential is similar for all concentrations. The maximum values of CO$_2$ current efficiencies, however, are different. Taking the results at 100°C for example, they are 68% (at 0.53 V) in 0.01 M acetaldehyde solution, while in 0.001 M acetaldehyde solution, they are 85% (at 0.49 V), respectively (all values for the positive-going scan).
Hence, for all concentrations the current efficiencies for CO$_2$ formation at 100°C and at 0.6 V in the positive-going scan are in the range between 50% and 60%. At higher potentials, the oxidation of acetaldehyde on the OH$_{ad}$/oxide covered surface produces large amounts of incomplete oxidation species (acetic acid) in 0.1 M and 0.01 M acetaldehyde solution. For very low acetaldehyde concentrations (1 mM), however, the reaction rate becomes significantly lower, which in turn leads to a visible oxide reduction peak in the subsequent negative-going scan (Fig. 4.3d).

The potential-dependent variation of the current efficiency for CO$_2$ formation in the acetaldehyde oxidation confirms that both the overall and partial reaction rates are controlled by the potential-dependent composition and coverage of the adlayer and by potential effects on the kinetically limited surface processes. At lower potentials (<0.5 V), the coverage of adsorbed C$_1$ species resulting from dissociative acetaldehyde decomposition is higher and inhibits the onset of acetaldehyde oxidation; at medium potentials (0.5 V ≤ E ≤ 0.7 V), the coverage of CO$_{ad}$ decreases due to CO$_{ad}$ oxidation, and at even more positive potentials (E > 0.7 V), the coverage of CO$_{ad}$ decreases further, due to more efficient CO$_{ad}$ oxidation and decreasing CO$_{ad}$ formation (C-C bond dissociation) on the oxy-species covered surface. The latter results in the change of the selectivity towards acetic acid formation, in agreement with the observation of adsorbed acetate species during acetaldehyde oxidation at high potentials by FTIRS [3,20] or SERS [28] measurements.

### 4.2.2 Potentiostatic oxidation of acetaldehyde

In order to deconvolute kinetic (reaction rate) and dynamic (linear variation of the electrode potential) effects, which both contribute to the potentiodynamic measurements, and to avoid effects caused by different coverages of the adsorbed species depending on the potential scan direction, we performed a series of potentiostatic experiments, monitoring simultaneously both the Faradaic current (Fig. 4.4a) and the mass spectrometric ion current for CO$_2$ formation (m/z = 44, Fig. 4.4b) at different constant electrode potentials and different reaction temperatures in 0.1 M acetaldehyde solution. The resulting current efficiencies for CO$_2$ formation are plotted in Fig. 4.4c (for details see Chapter 2).
For all temperatures, both Faradaic current (Fig. 4.4a) and the mass spectrometric current for CO$_2$ formation (m/z = 44, Fig. 4.4b) are below detection limit at potentials below 0.4 V. This agrees fully with the results obtained in potentiodynamic measurements (see section...
4.2.1), where acetaldehyde electrooxidation was inhibited below 0.4 V at 100°C and below about 0.45 V at 23°C, due to formation of strongly adsorbed species resulting from dissociative acetaldehyde adsorption.

Small Faradaic currents as well as mass spectrometric CO$_2$ signals were detected at 0.5 V at higher temperatures ($\geq$ 80°C, see insets in Figs. 4a,b), reflecting the thermal activation of the reaction under these conditions. (The current efficiencies for CO$_2$ formation below 80°C at 0.5 V are not shown in the figures because of the poor signal-to-noise ratio.) At 0.6 V, the Faradaic current for acetaldehyde oxidation increases steeply after the potential step, followed by a corresponding increase in the mass spectrometric current for CO$_2$ formation. At 0.7 V, the Faradaic current first increases and then decreases steadily until approaching a stable value after about 300 s. The corresponding mass spectrometric CO$_2$ signals closely follow the Faradaic current transients. The initial maximum in the CO$_2$ ion current signal is attributed to the fast oxidation of the CO$_{ad}$ which was produced at lower potential, before the potential step. Similar series of potentiostatic measurements were performed also in 0.01 M (Fig. 4.5) and in 0.001 M (Fig. 4.6) acetaldehyde solution to evaluate the effect of acetaldehyde concentration on the activity and selectivity of the acetaldehyde oxidation reaction under otherwise identical reaction conditions (temperature, potential, catalyst loading, electrolyte flow rate).

The general profiles of the current transients for constant potential oxidation for the dilute solutions are rather similar to those in 0.1 M acetaldehyde solution discussed above. While, the steady-state Faradaic currents as well as the CO$_2$ ion currents obtained under steady-state conditions are different. Furthermore, there are distinct differences in the potential dependence at different concentrations. While the steady-state Faradaic current increases by factors of 6.7 and 4.7 when going from 0.5 to 0.6 V and from 0.6 to 0.7 V, respectively, in 0.1 M acetaldehyde solution, the respective values are 5.6/1.5 and 1/0.7 in 0.01 M and 1 mM acetaldehyde solution (all at 100°C). A similar comparison of the corresponding CO$_2$ ion signals results in a comparable trend for 0.1 M acetaldehyde solution, while for 0.01 M acetaldehyde solution, the signal decreases when going from 0.6 V to 0.7 V. Finally, for 0.001 M acetaldehyde solution, this signal decreases already when going from 0.5 V to 0.6 V, opposite to the tendency in the Faradaic current, and going to 0.7 V, also the CO$_2$ formation...
ion current continues to decrease, following the behavior of the Faradaic current, but more pronounced.

Figure 4.5  Simultaneously recorded transients of the Faradaic current (a) and the CO$_2$ ion currents for m/z=44 (b), and the corresponding current efficiency for CO$_2$ formation (c) during potentiostatic oxidation of acetaldehyde on a Pt/Vulcan catalyst in 0.01 M acetaldehyde solution. Catalyst loading 40 $\mu$g$_{Pt}$ cm$^{-2}$, electrolyte flow rate 15 $\mu$l s$^{-1}$
We attribute these distinct differences in the behavior of the Faradaic current and the corresponding \( \text{CO}_2 \) ion current with acetaldehyde concentration and potential to differences in the composition and coverages of the adlayer, which in turn will affect the activity and selectivity of the reaction.

![Figure 4.6](image)

**Figure 4.6** Simultaneously recorded transients of the Faradaic current (a) and the \( \text{CO}_2 \) ion currents for m/z=44 (b), and the corresponding current efficiency for \( \text{CO}_2 \) formation (c) during potentiostatic oxidation of acetaldehyde on a Pt/Vulcan catalyst in 0.001 M acetaldehyde solution. Catalyst loading 40 \( \mu \text{gPt} \text{ cm}^{-2} \), electrolyte flow rate 15 \( \mu \text{l s}^{-1} \).
The corresponding current efficiencies for CO$_2$ formation, calculated from the steady-state currents at about 300 s, are listed in Table 4.1. For 0.1 M acetaldehyde solution, this increases up to ~80% at 100°C (0.5 V). At 0.6 V, the CO$_2$ current efficiencies are generally lower than at the lower potential (0.5 V), increasing from 7% at r.t. to 39% at 100°C, while the absolute currents are much higher. The increase of the CO$_2$ current efficiency with increasing temperature and decreasing potential (Table 4.1) shows a tendency with (i) decreasing potential (39 % at 0.6 V vs. 15% at 0.7 V, both at 100 °C) and (ii) increasing temperature (7% at 23°C vs. 39 % at 100°C, both at 0.6 V and 4% at 23°C vs. 15 % at 100°C, both at 0.7 V) resembles previous findings for the oxidation of ethanol or ethylene glycol on a Pt/C catalyst [21,39]. The temperature dependence and its implications will be discussed in detail in section 4.2.4.

Comparing the steady-state current efficiencies for CO$_2$ formation at constant potentials with the results obtained in potentiodynamic measurements at the same potential shows significant discrepancies. For reaction in 0.1 M acetaldehyde solution at 100°C and 0.6 V, the corresponding current efficiency is about 40% in potentiostatic measurements vs. ~60% in potentiodynamic measurements. The difference between these two measurements simply reflects the differences in the adlayer composition and coverage and their effect on the selectivity of the reaction.

For 0.01 M acetaldehyde solution, the resulting current efficiencies for CO$_2$ formation are comparable to those in 0.1 M solution, yielding values between ca. 10% at 23°C and ~40% at 100°C at 0.6 V (7% and 39% in 0.1 M solution).

Interestingly, the CO$_2$ current efficiencies decrease when going to 0.001 M acetaldehyde solutions, where we obtain values between 6% (23°C) and 30% (100°C) at 0.6 V (see Table 4.1).

Distinct concentration effects on the CO$_2$ current efficiency were observed also for ethanol oxidation on similar Pt/C catalyst electrodes, and at least partly attributed to transport effects, to the higher chance of re-adsorption and further reaction of the incomplete reaction product (acetaldehyde) to CO$_2$ in more dilute solutions [21] (‘desorption-re-adsorption-further reaction’ concept, see refs. [55-57]).
For the present case, contributions from re-adsorption of incomplete oxidation products can be excluded, since the only incomplete oxidation product, acetic acid, does not react further at present reaction conditions (see next section).

In this case, the variation of the current efficiency upon changes in the acetaldehyde concentration can only be due to differences in the composition and (partial) coverage of the adlayer in different reaction solutions, which directly affects the selectivity for C-C bond breaking vs. oxidation of the functional –CHO group. The influence of the adlayer on the selectivity is reflected also by the significant difference in CO\textsubscript{2} current efficiencies and hence in selectivity obtained in potentiostatic and potentiodynamic measurements. In the latter case, the convolution of potential and time effects results in a different adlayer composition than obtained under steady-state conditions at constant potential. Similar effects are also responsible for the variation of the CO\textsubscript{2} current efficiency with time during the reaction transients, which are particularly pronounced at low potential (0.5 V).

| Table 4.1   Steady-state current efficiencies for CO\textsubscript{2} formation (in percent) during potentiostatic acetaldehyde oxidation at different concentrations, potentials and temperatures. |
|-----------------|-----------------|-----------------|-----------------|
| T / °C          | 0.1 M Acetaldehyde | 0.01 M Acetaldehyde | 0.001 M Acetaldehyde |
| 23              | 7 ± 0.2          | 4 ± 0.1          | 9 ± 0.4          |
| 40              | 11 ± 0.6         | 5 ± 0.3          | 15 ± 0.7         |
| 60              | 20 ± 1           | 7 ± 0.3          | 21 ± 1           |
| 80              | 27 ± 1           | 9 ± 0.5          | 29 ± 2           |
| 100             | 39 ± 2           | 15 ± 0.8         | 41 ± 3           |
Increasing the potential to 0.7 V results in a significant decrease of the CO$_2$ current efficiencies for all concentrations and temperatures, without modifying the general trends for the temperature and concentration dependence discussed above. As will be discussed in more detail, in section 4.2.4, we associate this with a gradual change in the rate limiting step, from CO$_{ad}$ oxidation at lower potentials to C-C bond breaking at higher potentials. This in turn results in distinct changes in the adlayer composition, in particular in the coverage of reaction inhibiting CO$_{ad}$ species.

In total, the potentiostatic measurements revealed comparable trends in the reactivity and CO$_2$ selectivity as obtained in the potentiodynamic measurements; on a quantitative scale, however, the data differ significantly. This is attributed to the significant difference in the adlayer coverages and compositions in the two cases. Since the steady-state values obtained under potentiostatic conditions are free from dynamic variation in the adlayer, they are much better suited for comparison with fuel cell measurements.

### 4.2.3 Potentiostatic oxidation of acetic acid

In order to quantitatively determine the CO$_2$ formation in acetic acid oxidation under steady-state reaction conditions, a series of potentiostatic experiments were performed, monitoring the Faradaic current (Fig. 4.7a) and the mass spectrometric ion current for CO$_2$ formation (at m/z = 44, Fig. 7b) at different electrode potentials (from 0.2 V to 0.7 V) and different reaction temperatures. Because of the very low oxidation rates, measurements were performed only at temperatures ≥70°C and for 0.1 M acetic acid concentration and the corresponding data were corrected (for details see Chapter 2-experimental part).

At temperatures below 90°C, both the Faradaic current (Fig. 4.7a) and the mass spectrometric ion current for CO$_2$ formation (m/z = 44, Fig. 4.7b) are extremely low compared with the current in acetaldehyde oxidation, which shows that acetic acid is very stable towards C-C bond splitting and oxidation to CO$_2$ under these conditions. These results agree with previous findings for acetic acid (1 M acetic acid solution) oxidation at different temperatures (101°C, 152°C, 195°C and 249°C) on a Pt electrode, where measurable rates were observed only at temperatures above 200°C [32]. At 100°C, the Faradaic current and ion signal increased significantly, though their absolute values are still much lower than those for
acetaldehyde oxidation (Fig. 4.4) or ethanol oxidation [21]. Thus, contributions from acetic acid oxidation can be neglected in those reactions under present reaction conditions, i.e., oxidation of acetic acid formed by incomplete oxidation of ethanol or acetaldehyde can be neglected under present reaction conditions, at temperatures up to 100°C and on supported Pt catalysts. This agrees with the general perception that formation of acetic acid is a dead end in ethanol oxidation [19,20,31,58].

Figure 4.7  Simultaneously recorded transients of the Faradaic current (a) and the CO$_2$ ion currents for m/z=44 (b) during potentiostatic oxidation of acetic acid on a Pt/Vulcan catalyst in 0.1 M acetic acid solution at elevated temperatures (temperatures see figure). Catalyst loading 40 µg$_{Pt}$/cm$^2$, electrolyte flow rate 15 µl s$^{-1}$. 
4.2.4 Apparent activation energies

The apparent activation energies for the overall acetaldehyde oxidation reaction for the complete oxidation of acetaldehyde to CO$_2$, $E_a$ and $E_a$(CO$_2$), respectively, which were derived from the Arrhenius plots of the steady-state Faradaic currents and of the steady-state mass spectrometric ion currents at m/z=44 for different acetaldehyde concentrations and at the respective reaction potentials (Fig. 4.8), are listed in Table 4.2 (for details see Chapter 2). Furthermore, we also calculated the apparent activation energy for the incomplete oxidation of acetaldehyde to acetic acid from the Arrhenius plots for the partial oxidation current for acetic acid formation. The latter were calculated from the difference between the total reaction current and the partial reaction current of the complete oxidation to CO$_2$ (Fig. 4.9).

![Figure 4.8](image-url)  

**Figure 4.8** Arrhenius plots of the overall acetaldehyde oxidation rate (Faradaic current) of the complete oxidation of acetaldehyde to CO$_2$ (partial current for CO$_2$ formation) and of the incomplete oxidation to acetic acid (with assumption the products for acetaldehyde oxidation are only CO$_2$ and acetic acid) in 0.1 M acetaldehyde solution (a), 0.01 M acetaldehyde solution (b) and 0.001 M acetaldehyde solution (c) at different potentials (for potentials see figure). The precision in the current measurements is approximately ±15% in the Faradaic currents and ±9% in the mass spectrometric CO$_2$ signals. Electrolyte flow rate: 15 µl s$^{-1}$; catalyst loading 40 µg/cm$^2$. 
The linear decay of the logarithmic oxidation rates with 1/T implies that the rate determining step does not change with temperature. One has to keep in mind, however, that the overall reaction contains contributions from C-C bond splitting and CO₂ formation as well as from incomplete acetaldehyde oxidation to acetic acid, and even the incomplete reaction to acetic acid contains more than one reaction step. Therefore, these other reaction steps and also effects of the adlayer coverage and composition have to be considered in the complete reaction kinetics. This is most obvious for the overall oxidation of acetaldehyde. Here we know that the CO₂ current efficiency increases with increasing temperature and therefore the contributions of the two pathways change with temperature. Therefore, the measured barrier can not be associated with a single reaction step, but is an apparent barrier value reflecting the overall temperature dependence of the reaction network (Table 4.3).

<table>
<thead>
<tr>
<th>E / V</th>
<th>E_a / E_r (CO₂)</th>
<th>E_a / E_r (C₂H₄O₂)</th>
<th>E_a / E_r (CO₂)</th>
<th>E_a / E_r (C₂H₄O₂)</th>
<th>E_a / E_r (CO₂)</th>
<th>E_a / E_r (C₂H₄O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>32 ± 2 / 39 ± 2</td>
<td>27 ± 3</td>
<td>34 ± 2</td>
<td>40 ± 2</td>
<td>27 ± 2</td>
<td>33 ± 1</td>
</tr>
<tr>
<td>0.7</td>
<td>27 ± 1</td>
<td>42 ± 1</td>
<td>25 ± 1</td>
<td>42 ± 2</td>
<td>26 ± 3</td>
<td>26 ± 1</td>
</tr>
</tbody>
</table>

The close similarity between the values of the apparent activation barrier for incomplete oxidation to acetic acid at different acetaldehyde concentrations (27 ± 3 kJ mol⁻¹ at 0.6 V and 26 ± 3 kJ mol⁻¹ at 0.7 V) and for complete oxidation to CO₂ (39 ± 3 kJ mol⁻¹ at 0.6 and 42 ± 3 kJ mol⁻¹ at 0.7 V) indicates that the temperature dependence of the rate limiting step in these reaction pathways is largely independent of the acetaldehyde concentration. For the overall reaction, the close similarity of the values of \(E_a\) (33 ± 3 kJ mol⁻¹ at 0.6 V and 29 ± 3 kJ mol⁻¹ at 0.7 V)
at 0.7 V) for different acetaldehyde concentrations seem to indicate a similar situation; in this case, however, it reflects the temperature dependence of the entire reaction network with its two reaction pathways (see above discussion). In a more detailed discussion, one has to add that also the temperature dependence of the incomplete oxidation reaction to acetic acid may be dominated by the removal of CO\textsubscript{ad}, via the steady-state coverage of CO\textsubscript{ad}, and hence by OH\textsubscript{ad} formation and reaction with CO\textsubscript{ad}. This step can be dominant if the reaction is limited by the number of vacant sites available for acetaldehyde adsorption and subsequent dissociation.

Finally it should be noted that the effective activation energy for catalytic gas phase oxidation of acetaldehyde, using O\textsubscript{2} as oxidant, is significantly higher than the value determined here for acetaldehyde oxidation, with about 55 kJ mol\textsuperscript{-1} \cite{59} vs. about 40 kJ mol\textsuperscript{-1} in present work.

The potential dependence of the apparent activation energies is characterized by a subtle decrease of the values for \(E_a(CH_3COOH)\) and a similar size increase of \(E_a(CO_2)\) when going from 0.6 V to 0.7 V reaction potential. In total, this results in a comparable size decrease of the apparent activation barrier \(E_a\) for the overall reaction (see Table 4.2). The combination of a decreasing apparent activation energy for acetic acid formation and increasing apparent activation energy for CO\textsubscript{2} formation at higher potential leads to a change in the selectivity of the reaction towards a predominant acetic acid formation at higher potential, which is reflected by the decrease in current efficiency for CO\textsubscript{2} formation with increasing potential. We assume that these changes result at least partly from a gradual transition in the rate limiting step with potential. At lower potentials, oxidative removal of CO\textsubscript{ad} which is strongly influenced by the potential dependent OH\textsubscript{ad} formation, is rate limiting, while at higher potential CO\textsubscript{ad} oxidation is increasingly faster and C-C bond rupture becomes rate limiting. If the latter process is associated with a higher reaction barrier than OH\textsubscript{ad} formation / CO\textsubscript{ad} oxidation, this change in the rate limiting step results in the observed increase of the apparent activation energy for CO\textsubscript{2} with increasing potential. Furthermore, with increase in potential and temperatures, adsorption of oxy-species and sulfates reduces the number of larger adsorbate-free Pt ensembles required for the dissociative adsorption of acetaldehyde to form CO\textsubscript{ad}, while smaller ensembles sufficient for oxidizing the functional group to carboxyl are still available \cite{60}.\n
The still rather low values of $E_a(CO_2)$ obtained at 0.7 V, which was tentatively associated with C-C bond rupture, indicate that even for this reaction step the barrier is much smaller than the C-C bond energy (354.8±1.7 kJ mol$^{-1}$ in acetaldehyde [61], i.e., C-C bond breaking in adsorbed acetyl [20] proceeds in a highly correlated process, where simultaneous bond formation between the resulting fragments and the Pt nanoparticles leads to a pronounced reduction of the barrier compared to the C-C bond energy. The barrier for C-C bond rupture in acetaldehyde is significantly lower than the barrier for complete oxidation of ethanol to CO$_2$ at ~0.7 V under similar conditions (65 ± 3 kJ mol$^{-1}$ in 0.1 M ethanol solution) [21]. Apparently, in the latter case, simultaneous bond formation of the fragments with the Pt particles is less efficient than for adsorbed acetaldehyde, resulting in a higher barrier of the C-C bond rupture step. Investigating the mechanism of ethanol oxidation, especially the selectivity of this reaction, on different Pt surfaces with density functional theory based calculations, Wang and Liu calculated reaction barriers for C-C bond breaking of ethanol is 287.5 kJ mol$^{-1}$, while C-C for adsorbed acetyl this value is much lower (131.2 kJ mol$^{-1}$) [62]. They also found that CO$_2$ and acetic acid originate from the same surface intermediate, CH$_3$CO$_{ad}$, in agreement with previous experimental findings [20], and that C-C bond breaking occurs predominantly via strongly adsorbed CH$_2$CO or CHCO intermediates on defect sites rather than directly from CH$_3$CO$_{ad}$ on the flat Pt(111) terraces. The CH$_2$CO$_{ad}$ or CHCO$_{ad}$ intermediates were formed before by CH$_3$CO dehydrogenation.

The apparent activation energies for acetic acid oxidation, as measured by the Faradaic current and by the CO$_2$ mass spectrometric signal are in the range of ~115 - 180 kJmol$^{-1}$ (note that the mass spectrometric currents at 70 °C and 0.6/0.7 were too low to be reliably evaluated and therefore not used for the determination of the activation barrier). As expected from the fact that CO$_2$ is the only reaction product, the values for the activation energy determined from the Faradaic current and from the mass spectrometric CO$_2$ signal agree reasonably well. The high values indicate that in this case the simultaneous bond formation, together with C-C bond breaking is much less efficient than for Pt catalyzed C-C bond breaking in other molecules such as ethanol [21] or acetaldehyde (see above). To overcome the reaction barrier for acetic acid oxidation on a Pt electrode, much higher temperature (above 200 °C) are required according to the literature data [32].
Table 4.3  Apparent activation energies for the overall acetic acid oxidation (0.1 M) reaction (Faradaic current) and complete oxidation to CO$_2$ (CO$_2$ partial reaction current) at different potentials, determined from steady-state reaction currents.

<table>
<thead>
<tr>
<th>E / V</th>
<th>$E_a$ / kJ mol$^{-1}$</th>
<th>$E_a$ (CO$_2$) / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>115±8</td>
<td>118±13</td>
</tr>
<tr>
<td>0.6</td>
<td>173±6</td>
<td>223±20</td>
</tr>
<tr>
<td>0.7</td>
<td>157±18</td>
<td>209±39</td>
</tr>
</tbody>
</table>

The above data confirm the existing picture that formation of acetic acid during acetaldehyde oxidation, and similarly also for ethanol oxidation, is a ‘dead end’, where further oxidation is not possible under common reaction conditions [19,20,28,58]. C-C bond breaking has to occur in the preceding reaction steps, e.g., during interaction of the surface with adsorbed acetyl species [20]. Once acetic acid is formed, it is essentially stable even at 100°C.

### 4.2.5 Implications for direct ethanol fuel cell operation

The results reported in the previous sections have considerable implications on the understanding and optimization of DEFCs. Assuming that ethanol oxidation proceeds at least partly via formation of adsorbed acetaldehyde /acetyl species, which can subsequently desorb (acetaldehyde formation) or continue reaction to acetic acid or CO$_2$, the oxidation of acetaldehyde is a crucial step in the reaction sequence.
Figure 4.9 Arrhenius plots of the overall acetic acid oxidation rate (\(I_F\)) and of the complete oxidation of acetic acid to CO\(_2\) [\(I_{F(CO_2)}\)] in 0.1 M acetic acid solution at different potentials (potentials see figure). The mass spectrometric CO\(_2\) signal at 70 °C and 0.6 as well as at 0.7 V are too low to be reliably evaluated and therefore not shown. Electrolyte flow rate: 15 µl s\(^{-1}\); catalyst loading 40 µg\(_{Pt}\) cm\(^{-2}\).

First, it is important to note that increasing reaction temperatures not only result in a higher reaction rate, but, due to the higher activation barrier for complete oxidation of acetaldehyde to CO\(_2\) compared to its partial oxidation, also in a decreasing amount of acetic acid formation. Extrapolating the data in Fig. 4.8 to higher temperatures, one can estimate that under current reaction conditions and at 0.6 V, complete conversion to CO\(_2\) will be reached at about 364°C (0.1 M solution), provided there is no change in the reaction mechanism and rate determining pathways. For higher potentials, this temperature will shift to higher values (~ 340°C at 0.7 V). It is interesting to note that while acetaldehyde adsorption (CO\(_{ad}\) formation) on Pt is much more facile at ambient temperature and also less potential dependent that ethanol oxidation, the increase of the CO\(_2\) current efficiency is much steeper for ethanol oxidation, resulting in a much lower temperature for complete conversion to CO\(_2\) of ~175°C at 0.6 V (140°C at 0.5 V) [21].

Acetic acid formation has to be avoided at the stage of acetaldehyde/acetyl interaction with the active Pt nanoparticles, since once formed its later oxidation is essentially impossible under realistic fuel cell reaction conditions. Since ethanol oxidation is likely to proceed via
adsorbed acetyl / acetaldehyde formation, the selectivity of acetaldehyde oxidation to CO\textsubscript{2} is a prime objective in the optimization of anode catalysts for DEFCs.

Second, considering possible improvements in the anode catalyst, one has to keep in mind that this has to activate not only C-C bond breaking, but also the oxidative removal of the resulting adsorbed fragments CO\textsubscript{ad} and CH\textsubscript{x,ad} to CO\textsubscript{2}. Only if the removal of these species is not rate limiting, a further increase of the C-C bond breaking rate will lead to an overall improvement of the reaction kinetics, i.e., a higher oxidation current. Otherwise, the increasing steady-state coverage of CO\textsubscript{ad} and CH\textsubscript{x,ad} species will result in an effective decrease of the oxidation current. In that sense, catalysts with an improved activity for C-C bond breaking are not beneficial for the acetaldehyde oxidation reaction, unless they are also more active for oxidation of adsorbed CO\textsubscript{ad} and CH\textsubscript{x,ad} species. These conclusions are equally correct also for ethanol oxidation. In that sense, bimetallic catalysts with improved CO\textsubscript{ad} oxidation properties compared to Pt/C such as PtSn/C or PtRu/C [7,12,17,31] are beneficial for complete oxidation of ethanol or acetaldehyde to CO\textsubscript{2} only if they are also more active for C-C bond breaking. So far, this latter question is still open for reaction at elevated temperatures. Recently, Kowal et al. presented a Pt/Rh/SnO\textsubscript{2} catalyst, which according to their claims was more active in both partial reaction steps in ethanol oxidation and which may be a promising step forward [63, 64].

4.3 Conclusions

Potentiodynamic and potentiostatic DEMS measurements of the acetaldehyde and acetic acid oxidation reactions on carbon supported Pt/Vulcan thin-film catalyst electrodes performed under fuel cell relevant, but nevertheless well defined reaction and transport conditions (controlled electrolyte transport, continuous reaction, elevated temperatures and pressure) and on relevant materials (supported catalysts, 100% catalyst utilization), led to the following conclusions:

1. For acetaldehyde oxidation, both the overall reaction rate, as measured by the Faradaic current, and the rate for CO\textsubscript{2} formation increase significantly with increasing reaction temperature. The increase with temperature is more pronounced for complete oxidation to
CO₂ than for the overall acetaldehyde oxidation reaction. Correspondingly, the apparent activation energies are higher for CO₂ formation than for the overall reaction (39±2 kJ mol⁻¹ vs. 32±2 kJ mol⁻¹ in 0.1 M acetaldehyde solution, 0.6 V).

2. In the same way, also the current efficiency for CO₂ formation (during acetaldehyde oxidation) increases significantly with temperature, in particular at temperatures >60°C, from negligible CO₂ formation (7%) at room temperature under steady-state conditions to 39% at 100°C (0.6 V). Accordingly, the formation of the incomplete oxidation product acetic acid, which is dominant at ambient temperature, decreases significantly with temperature. High values of the current efficiency for CO₂ formation over the Pt/C catalyst can be reached, however, only at low potentials (0.5 V) and hence at rather low current densities (geometric surface area normalized current density): 81±3% at 0.16 mA cm⁻² (0.5 V, 0.1 M acetaldehyde solution), 93±4% at 0.34 mA cm⁻² (0.5 V, 0.01 M acetaldehyde solution), and 77±3% at 1.25 mA cm⁻² (0.5 V, 0.001 M acetaldehyde solution) (all at 100°C).

3. The activation energies for the overall reaction and for the pathway for CO₂ formation decrease slightly with potential, from 32±2 and 39±2 kJ mol⁻¹ at 0.6 V to 27±1 and 42±1 kJ mol⁻¹ at 0.7 V in 0.1 M solution, respectively. Correspondingly, also the current efficiencies for CO₂ formation decrease with increasing potential, e.g., from 39% (27%) at 0.6 V to 15% (9%) at 0.7 V at 100°C (80°C). The decrease in both quantities with potential is associated with the transition in the rate limiting step, from COₐd oxidation at lower potentials to C-C bond breaking (COₐd formation) at higher potential.

4. Contrary to ethanol oxidation, transport effects play only a limited role in acetaldehyde oxidation, since contributions from re-adsorption and further reaction of reactive reaction intermediates are negligible, due to the very low reactivity of acetic acid under present reaction conditions. They only come into play via different compositions of the adlayer, i.e., different coverages of different coexisting adsorbates during reaction in solutions of different reactant (acetaldehyde) concentration.

5. Significant differences between the CO₂ current efficiencies determined in potentiodynamic measurements and under steady-state conditions in potentiostatic measurements at similar potentials are explained by a combination of different effects specific for
potentiodynamic measurements: i) the convolution of potential and time effects in potentiodynamic measurements, which result in different adlayer coverages and compositions in both types of measurements at a given potential, and ii) the oxidation of adsorbed species pre-formed at other (lower) potentials, which leads to lower electron yields per CO₂ molecule formation compared to complete oxidation of acetaldehyde to CO₂. Due to these effects, only the CO₂ current efficiencies determined under steady-state conditions are reliable for quantitative comparison with fuel cell measurements and operation, while the validity of values determined in potentiodynamic measurements is limited to qualitative discussions of the trends.

6. From the linear correlation between ln r and 1/T over the full temperature range in the Arrhenius plots, both for the overall reaction and for the partial reactions (incomplete oxidation to acetic acid and complete oxidation to CO₂) we conclude that the rate limiting reaction steps in the two reaction pathways do not change with temperature, over the entire temperature scale.

7. Acetic acid is essentially inactive to further oxidation to CO₂ even at 100°C under present experimental condition. This goes along with a very high apparent activation energy for this reaction of between 110 and 200 kJ mol⁻¹, depending on the potential, which is much higher than the values for ethanol oxidation or acetaldehyde oxidation under identical reaction conditions.

For practical applications in a direct oxidation fuel cell it is important to note that improvements in the general activity of the acetaldehyde oxidation reaction require a higher activity of the respective catalyst in two reactions, in C-C bond breaking (COₐd formation) and in COₐd oxidation. If only one of these two partial reactions is accelerated, this will lead to rate limitations by the respective other partial reaction (C-C bond breaking at high potentials, COₐd surface blocking at lower potentials). This explains also the much smaller improvements reached by bimetallic catalysts for ethanol and acetaldehyde oxidation as compared to methanol oxidation.
Acknowledgements

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4.5 References


Chapter 5

Electrooxidation of ethanol on Pt-based and Pd-based catalysts in alkaline electrolyte under fuel cell relevant reaction and transport conditions
The content of the following section is based on the manuscript by S. Sun, Z. Jusys, and R.J. Behm, “Electrooxidation of ethanol on Pt-based and Pd-based catalysts in alkaline electrolyte under fuel cell relevant reaction and transport conditions”, which has already been submitted to the Journal of Power Sources. The corresponding figures and tables have been adapted to fit the layout of the thesis. The experimental description for the following section is represented in Chapter 2. The figures, tables and the corresponding descriptions shown in the following section are same as submitted. The majority of the data acquisitions, evaluation, graphing and writing of the manuscript were done by the author of this thesis.

Abstract

The electrooxidation of ethanol on Pt-based (Pt/C, PtRu black) and Pd-based (Pd/C, Pd/CeO$_2$/C) supported catalysts in alkaline solution was investigated under fuel cell relevant reaction and transport conditions, over a wide range of temperatures (from 23 to ~100°C) in a high temperature / high pressure (3 bar overpressure) flow cell under controlled transport conditions. Potentiodynamic and potentiostatic measurements on thin film catalyst electrodes reflect significant effects of the reaction temperature and potential. The addition of Ru to Pt and CeO$_2$ to Pd/C improves the tolerance with respect to catalyst poisoning, e.g., by CO$_{\text{ad}}$, at low potentials, while for higher potentials and especially at higher temperature the activity of the monometallic catalysts is higher. For reaction at relevant conditions (0.5 V, 80°C), the Pd/C catalyst exhibits the highest activity, both in terms of metal mass specific rates and of active surface area normalized rates, the addition of a second oxophilic component is beneficial only for lower potentials. The apparent activation energies for ethanol oxidation on the different catalysts, which are in the range of 11 - 32 kJ mol$^{-1}$ as determined from steady-state Faradaic current, vary significantly with potential.

5.1 Introduction

The electrooxidation of ethanol has attracted significant interest, both from fundamental reasons, as a model reaction for the electro-oxidation of small organic molecules, and because of its potential application in direct ethanol fuel cells [1-6]. For reaction in acidic electrolyte,
where most of the studies focused on, it was found that the reaction is kinetically hindered and requires a significant overpotential. Furthermore, efficient catalysis requires expensive noble metal catalysts [7,8]. In acidic medium, platinum is often considered to be the best monometallic catalyst for oxidation of hydrocarbon molecules with its characteristic ability for catalytic C-H bond cleavage, whereas CO$_{ad}$ oxidation on Pt electrodes requires a significant overpotential [5,9]. This is different for reaction in alkaline electrolyte, where overpotentials were found to be significantly lower and where inexpensive transition metal electrodes such as Ni and/or Ru were found to be highly active [10]. Recently, the interest in alkaline ethanol oxidation has been raised considerably by new developments in alkaline anion exchange membranes, which make alkaline ethanol oxidation fuel cells more feasible [11-14], and much of the research was addressed to transition metal electrodes, such as Ni, Au, Ag, Cu, Ru, Zn (also their combination with Pd or Pt) [10,15].

In the present paper, we report results of a comparative study on the EOR on three different carbon supported catalysts (Pt/C, Pd/C and Pd/CeO$_2$/C) and an unsupported PtRu catalyst (PtRu black). For better comparison with fuel cell reaction characteristics, the measurements were performed under fuel cell relevant reaction conditions, at elevated temperatures, up to 100°C, and pressure (3 bar overpressure) and under continuous controlled electrolyte transport.

Previous studies on ethanol oxidation (ethanol oxidation reaction - EOR) on different types of Pt-based catalysts (single crystalline and polycrystalline (pc) platinum and platinum alloys, carbon supported platinum and platinum alloy catalysts) in alkaline medium [16-22] revealed lower overpotentials for the removal of electrode poisoning species such as CO$_{ad}$ than in acidic electrolyte, due to the higher concentration of hydroxyl species [23]. Lai et al [19,21] reported a considerable enhancement of the EOR activity on a pc platinum electrode in 0.1 M NaOH solution ethanol as well as a negative shift of about 100 mV in the onset potential (~50 mV in peak potential) compared to that in 0.1 M HClO$_4$ solution for similar ethanol concentration (0.5 M). Jiang et al. [20] determined an increase of the EOR current density on a Pt/C catalyst by a factor of 4 (at 0.5 V vs. RHE) or 5 (at 0.6 V vs. RHE) in 0.1 M NaOH solution compared with that in 0.5 M H$_2$SO$_4$ solution (both cases 0.01 M ethanol) at room temperature, connected with a cathodic shift of the onset potential by about 80 mV. The
addition of Sn to Pt/C (PtSn/C) catalyst showed a negligible improvement in the EOR kinetics compared with a Pt/C catalyst in alkaline solution, in contrast to findings in acidic solution, where bimetallic PtSn catalysts are considered as most active catalysts [7,8,24-26]. A similarly small difference was observed also for a Pt$_3$Ru$_3$ catalyst, compared to a Pt/C catalyst, in the MOR kinetics in alkaline solution [27]. Also the product distribution in the EOR was much more favorable in alkaline than in acidic electrolyte. Rao et al. [17], who quantitatively determined the product distribution in a direct ethanol oxidation fuel cell by online mass spectrometry measurements, reported CO$_2$ current efficiencies in the order of 55% at a potential of 0.8 V vs. RHE and a temperature of 60°C on a Pt electrode in 0.2 M KOH containing 0.1 M EtOH, which is significantly higher than the CO$_2$ current efficiencies obtained in acidic media under similar conditions [17,28]).

Palladium is known as a poor electrocatalyst for alcohol oxidation in acidic medium, but shows a remarkable EOR activity in alkaline environment [22,29-38]. Zheng et al. [39] investigated the activity of Pd catalysts, employing different types of support, and compared it with that of a Pt/C catalyst (in 1 M KOH + 1 M EtOH). They found that a multiwall carbon nanotube (MWCNTs) supported Pd catalyst exhibited a higher activity, by a factor of 3, than the Pt/C catalyst. In order to improve the electrocatalytic activity and stability, oxide supports such as CeO$_2$ were added to the Pd/C catalyst [40], which increased the EOR activity in 1 M KOH containing 1 M ethanol compared to that of the pure Pd/C catalyst [33,40].

In the following, we will first present and discuss results of potentiodynamic (section 5.2.1) and potentiostatic (section 5.2.2) measurements in 0.5 M NaOH containing 0.1 M ethanol solutions on different thin film catalyst (Pt/C, Pd/C, Pd/CeO$_2$/C, PtRu black) electrodes. Subsequently, we will compare the mass specific and active surface area specific activities of the respective electrodes in the temperature range between 23°C and 80, respectively, at different potentials (section 5.2.3). Apparent activation energies for ethanol oxidation reaction in alkaline solution on the Pt- and Pd-based catalysts were derived under similar reaction condition and discussed in the last part (section 5.2.4).
5.2 Results and discussion

5.2.1 Potentiodynamic oxidation of ethanol on respective catalyst

Fig. 5.1 shows a series of potentiodynamic ethanol oxidation traces recorded during continuous potential cycling (10 mV s$^{-1}$ scan rate) in 0.5 M NaOH solution containing 0.1 M ethanol on different catalysts and at different temperatures (see figure): (a) Pt/C catalyst, (b) PtRu black, (c) Pd/C and (d) Pd/CeO$_2$/C catalysts, respectively.

![Fig. 5.1](image-url)

**Fig. 5.1** Positive-going scan (left panel) and negative-going scan (right panel) of CVs of the ethanol oxidation reaction during continuous potential cycling on different thin film catalyst electrodes in 0.1 M ethanol + 0.5 M NaOH solution pressurized with 3 bar N$_2$ overpressure at elevated temperatures (temperatures see figure): (a) Pt/C catalyst, (b) PtRu black catalyst, (c) Pd/C catalyst and (d) Pd/CeO$_2$/C catalyst. Inset: Onset of the reaction magnified Faradaic current. Potential window: Pt/C and Pd/C catalysts: 0.06V - 1.16V; Pd/CeO$_2$/C catalyst: 0.1V–1.2V; PtRu black catalyst: 0.06V - 0.8V. Potential scan rate 10 mV s$^{-1}$, electrolyte flow rate 15 µl s$^{-1}$, arrows indicate the direction of potential scan.
For more clarity, the positive-going scans and the negative-going scans are displayed in two separate panels. (It should be noted that the absence of curves for Pt/C and for Pd/C catalysts in the negative-going scan at 100°C is due to instabilities / oscillations.) In addition, the traces recorded at room temperature are also shown with higher magnification (magnifications see Figures). Furthermore, the onset of the Faradaic currents is shown in the insets in an expanded current scale.

For the Pt/C catalyst (Fig.5.1a) at 23°C, the general pattern of the Faradaic current is similar to that reported previously for a similar Pt/C catalyst and under similar reaction conditions [20]. At potentials below about 0.28 V (see inset), the electrooxidation of ethanol is essentially inhibited, which is attributed to the presence of a reaction inhibiting adlayer of adsorbed residues resulting from dissociative ethanol adsorption formed at lower potentials in the preceding negative-going scan. These are mainly CO_{ad} and adsorbed hydrocarbon residues [19,21]. However, compared to results reported previously in acidic electrolyte (same transport and reaction conditions, 0.5 M H_{2}SO_{4} solution [41]), the onset potential is shifted to lower values (0.28 V in alkaline electrolyte vs. 0.35 V in acidic electrolyte at 23°C), which is attributed to the more facile OH^{-} adsorption from alkaline electrolyte as compared to OH_{ad} formation via H_{2}O splitting in acidic electrolyte [27,47,48].

At potentials above 0.28 V, the Faradaic current increases, which correlates with the onset of CO_{ad} oxidation on Pt electrodes in alkaline electrolyte [49], passes through a maximum at ~0.56 V, and then decreases with further increasing potential through an ill-resolved shoulder between 0.65 and 0.75 V (see magnified current trace). This agrees well with previous reports which concluded that CO_{ad} oxidation on a Pt electrode in alkaline solution proceeds via a Langmuir-Hinshelwood mechanism [49–53]. Then the Faradaic current continuously decays until reaching the detection limit at a potential above 0.9 V. This decay is related to the increasing coverage of OH_{ad} / surface oxide species, which inhibit the EOR.

With increasing the temperature, we observed the following characteristic changes in the Faradaic current characteristics in the positive-going scan: i) the peak current increases from 0.54 mA (23°C) to 2.7 mA (90°C); ii) the onset potential shifts negatively, from ~0.28 V at 23°C to ~0.24 V at 90°C; iii) the potential of the peak maximum shifts from ~0.56 V at 23°C to ~0.52 V at 90°C; and iv) the ratio between the peak current and the current in the ill-
resolved shoulder increases slightly with temperature. The obvious thermal activation of the EOR, which agrees with similar tendencies in the temperature dependent EOR in acid electrolyte [41], can result from different effects, including the activation of the C-C dissociation, partial thermal desorption of CO\text{ad} species formed during the reaction [54], and/or activation of the reaction between ethanol adsorbate and oxygen-containing species [55-57].

The general appearance of the Faradaic current in the negative-going scans (Fig. 5.1a, right panel) resembles that in the positive-going scans (Fig. 5.1a, left panel). Starting from high potentials, the Faradaic currents are inhibited at potentials above ~0.8 V at 23°C. Scanning the potential negatively, the current increases until reaching its maximum at ca. 0.56 V, decreases through an ill-resolved shoulder at ca. 0.37 V and finally reaches its detection limit. With increasing temperature, the Faradaic current peak develops a distinct double-peak characteristic (the shoulder becomes more pronounced) and the peak current increases about four-fold compared to that at ambient temperature. Furthermore, the ratio of the peak currents in the negative-going scan and in the positive-going scan (\(I_{F,n}/I_{F,p}\)) increases from 0.7 at 23°C to 0.8 at 90°C, most likely due to differences in the respective coverages of adsorbed ethanol decomposition products formed at lower potentials in the preceding negative-going scans. Similar observations of a lower peak current during the negative-going scan than in the positive-going scan (\(I_{F,n}/I_{F,p}<1\)) were reported for the oxidation of methanol on a polycrystalline Pt electrode in alkaline solution, where the \(I_{F,n}/I_{F,p}\) ratio was used as an estimate of the poisoning effect, which caused a decrease of the current in the negative-going scan and was ascribed to (bi)carbonate formation/adsorption [58].

For the PtRu black catalyst electrode (Fig. 5.1b), the general appearance of the Faradaic current profiles and their variation with increasing temperature is rather similar to that of the Pt/C catalyst. It should be noted that the positive potential limit for the PtRu black catalyst was set to 0.8 V to avoid leaching of the Ru component. The main temperature effects are as follows, i) the peak current in the positive-going scan increases from 0.15 mA (23°C) to 1.25 mA (100°C), which is somewhat lower than the corresponding current values on the Pt/C catalyst; ii) the onset potential shifts negatively, from ~0.25 V at 23°C to ~0.20 V at 100°C. Compared with the onset value of 0.3 V on a PtRu/C catalyst electrode in 0.5 M \(\text{H}_2\text{SO}_4\).
solution (0.1 M ethanol, room temperature) [59], the shift in pH from 0.3 to 13.7 results in a potential shift of ~50 mV negatively. iii) Different from the Pt/C catalyst, the Faradaic current shows a single broad peak, and the peak potential shifts only by ca. 30 mV from ~0.58 V at 23°C to ~0.55 V at 100°C. The current-potential profiles closely resemble also those reported for methanol oxidation on a PtRu alloy catalyst at different temperatures in alkaline solution [60]. The lower onset potential compared to a Pt/C catalyst reflects the easier formation of oxygen-containing species on the Ru sites at low potentials, together with modifications of the Pt electronic states by alloyed Ru resulting in a weaker adsorbate bonding to Pt [61,62]. Similar thermally induce shifts of the onset potential were observed in earlier temperature dependent studies of methanol oxidation on PtRu alloy electrodes in acid [63] and in alkaline electrolyte [27]. The lower Faradaic current compared to that on the Pt/C catalyst, illustrated, e.g., by a peak current of 0.8 mA on PtRu black vs. 2.3 mA on the Pt/C catalyst (both at 80°C), points to kinetic hindrance of the EOR on the PtRu catalyst. This is most easily explained by a slower ethanol adsorption/dehydrogenation reaction on Ru sites or on Pt sites modified by electronic ligand and strain effects leading to a modification in the activity. A similar observation was reported for methanol electrooxidation on a PtRu/C catalyst in both alkaline and acidic solution [27].

The negative-going Faradaic current scans resemble the positive-going scans in their general appearance (Fig. 5.1b), the $I_{F,n}/I_{F,p}$ ratios remain well below 1 (0.53 at 23°C, 0.78 at 100°C). Most likely this reflects a considerable influence of the high CO$_{ad}$ coverage present in the initial stage of the positive-going scan, while in the initial phase of the negative-going scan the CO$_{ad}$ coverage is negligible. This leads to rather high CO$_{ad}$ coverages at higher potentials, in the potential range of the peak maximum, in the positive going scan, while in the negative-going scan the CO$_{ad}$ coverage under these conditions, which can arise only from C-C bond splitting /CO$_{ad}$ formation at these potentials, is much lower. In addition, the different composition / coverage of the adlayer may affect also the selectivity of the reaction [41], with direct consequences for the measured Faradaic current.

For the Pd/C catalyst (Fig. 5.1c), the corresponding cyclic voltammograms exhibit similar characteristics as obtained for the Pt/C catalyst (Fig. 5.1a). At 23°C and in the positive-going scan, the Faradaic current starts at ca. 0.32 V, passes through a maximum at about 0.74 V, and
then decreases with further increasing potential, until reaching its minimum value at about 1.0 V. The decrease in Faradaic current is related to the formation of a OH adlayer or Pd oxide layer on the electrode surface [36,64-66]. Increasing the temperature, the Faradaic current increases and the onset potential shifts to lower values, reaching 0.27 V at 100°C. This trend resembles that on the Pt-based catalysts (Fig. 5.1a for Pt/C, Fig. 5.1b for the PtRu black catalyst). In the subsequent negative-going scan, the general current-potential profile with a sharp peak occurs at ca. 0.66 V (at 23°C), whose peak potential shifts to about 0.7 V (at 80°C). For this catalyst, the current peak in the negative-going scan is higher than that in the positive-going scan, the corresponding I_{F,n}/I_{F,p} ratio decreases from 1.7 at 23°C to 1.1 at 80°C. The thermally induced decrease of the peak current ratio may be due to a more effective thermal activation of the reaction between adsorbed ethanol adsorbates and oxygen-containing species in the positive-going scan, with an increase of I_F by a factor of 4.2, as compared to the adsorbate formation/removal in the negative-going scan, with an increase of I_F by a factor of 2.7, going from 23 to 80°C.

Finally, for the Pd/CeO_2/C catalyst (Fig. 5.1d), the cyclic voltammograms resemble those obtained for the Pd/C catalyst in their general appearance, but there are some distinct differences. First, the onset potential is shifted negatively, from ~0.32 V for the Pd/C catalyst at 23°C to ~0.2 V. Obviously, the presence of CeO_2 promotes the oxidation of ethanol decomposition products at lower potential, which can be explained by the ability of ceria and ceria related materials to store and release oxygen [67]. It can provide O-containing species, which facilitate the oxidation of reaction inhibiting adspecies. With increasing reaction temperature, the onset potential shifts to slightly lower values, reaching ~0.15 V at 100°C. The same is true for the peak potential, which shifts from ~0.7 V at 23°C to 0.66 V at 100°C. After passing through the maximum, the current decays slowly and reaches a plateau at ~1.0 V at 23°C (at ~0.9 V at 100°C). Hence, similar to the Pd/C catalyst, Pd/CeO_2/C catalyzes the EOR at high potentials, where the metal surface is covered of OH_{ad} or oxide. This tendency is most pronounced for the present catalyst. With increasing temperature, the peak current for ethanol oxidation increases, by a factor of 5.4 from 23°C to 100°C. In the negative-going scan, the general appearance of the current trace is rather similar to that in the positive going scans.
The peak currents are almost identical in the two scan directions, with the ratio $I_{F,n}/I_{F,p}$ decreasing from 1.14 at 23°C to 1.03 at 100°C, reflecting a more effective thermal activation of the reaction in the positive-going scan (an increase by factor of 5.5 in the positive-going scan vs. 4.9 in the negative-going scan, both comparing $I_F$ at 100°C with that at 23°C). Following the arguments given above for Pt/C, the $I_{F,n}/I_{F,p} ≈ 1$ indicates that the influence of the adlayer, including coverage and composition, on the overall Faradaic current is little.

The main results of the potentiodynamic EOR measurements in alkaline solution over the above catalysts can be summarized as follows:

(i) For all catalysts, the activity for the EOR in alkaline electrolyte is higher than in acid electrolyte. For the Pt/C and PtRu/C catalysts, this goes along with a shift of the onset potential to lower potentials when comparing the reaction in alkaline and acid solution. For the Pd/C and Pd/CeO$_2$/C catalysts, which are essentially inactive in acidic solution, we find a very high (Pd/C) or significant (Pd/CeO$_2$/C) activity for catalyzing the EOR in alkaline electrolyte.

(ii) Addition of oxophilic components such as Ru in PtRu black and CeO$_2$ in Pd/CeO$_2$/C, shifts the onset potential to lower values, which reflects their ability to promote the oxidation of reaction inhibiting CO$_{ad}$ species or other reaction side products / intermediates at low potentials. On the other hand, the peak currents are significantly reduced upon addition of these oxophilic species compared with the corresponding monometallic catalysts, as expected for additives that are little active for the dehydrogenation of ethanol molecules and C-C bond cleavage.

(iii) The influence of the state of the catalyst surface (oxidation state, nature and coverage of adsorbed reaction intermediates/side products) is reflected by the more or less pronounced differences in peak shape and peak current in the positive-going and negative-going scan. This is indicated by the ratio of the peak currents, $I_{F,n}/I_{F,p}$, which is <1 for the Pt-based (0.69 for Pt/C catalyst, 0.63 for PtRu black at 80°C) and >1 for the Pd-based catalysts (1.1 for Pd/C and 1.3 for Pd/CeO$_2$/C at 80°C). Increasing the temperature leads to an increase of the $I_{F,n}/I_{F,p}$ ratio for the Pt/C and PtRu black electrodes, and a decrease for the Pd/C and Pd/CeO$_2$/C catalysts.

(iv) The temperature effects in the cyclic voltammograms are approximately similar for all catalysts. While the general shape of the CVs is largely maintained, the peak heights increase
significantly, by factors between 3 and 5 when comparing the peak current in the positive-going scan at 80°C with that at 23°C.

5.2.2 Potentiostatic oxidation of ethanol

In order to separate kinetic (reaction rate) and dynamic (temporal variation of the electrode potential) contributions to the Faradaic current in the potentiodynamic measurements, e.g., via time and potential dependent adsorbed species coverages, we performed a series of potentiostatic experiments (for details see Experimental part of Chapter 2) at different electrode potentials and different reaction temperatures in 0.5 M NaOH solution containing 0.1 M ethanol (Fig. 5.2). Generally, the Faradaic current was followed over 300 s at each potential, and the potential was increased stepwise. Only for the Pt/C catalyst, this was extended to 900 s to reach steady-state conditions, and all transients started from 0.06 V (for details see Chapter 2). Arrhenius plots of the steady-state Faradaic currents for determining the apparent activation energies are presented and discussed in section 5.2.4.

For the Pt/C catalyst (Fig. 5.2a), the general shape of the ethanol oxidation transients can be described by a steep initial increase of the Faradaic current after the potential step, followed by a slower, approximately exponential decrease, to approach the steady-state current. The initial spike, which is partly due to double-layer charging, as well as the currents in the later stages of the transients, depend sensitively on temperature and reaction potential. The profiles of the initial current maximum become progressively sharper with increasing temperature, with the rapid increase of the Faradaic current at higher temperature followed by an almost equally fast decay, due to the rapid development of reaction inhibiting adsorbed species such as adsorbed CO or other strongly bonded species originating from the dissociative adsorption of ethanol under these conditions [19,21], while at 23°C the Faradaic current increases slowly followed by a slow decay.

At 0.4 and 0.5 V (Fig. 5.2a), the reaction exhibits an unusual temperature dependence: at lower temperatures, from 23 to 80°C, the steady-state Faradaic current decreases with increasing temperature, and only when going 90°C, it increases again. This is possibly due a change in the origin of the rate limitation, from site blocking due to increasing CO_{ad} formation and coverage at lower temperatures to CO_{ad} formation at 90°C.
Comparable potentiostatic measurements of the ethanol oxidation reaction on a Pt/C catalyst at 0.4, 0.5 and 0.6 V (15 min for each step) over the temperature range from 22 to 60°C were reported recently [20]. For reaction at 0.4 V and 0.5 V, these authors observed that the oxidation current density increased when raising the temperature from 22 to 40°C, and then decreased upon a further temperature increase to 60°C. They explained this by the temperature dependent coverage of poisoning species on the catalyst surface, which increases with increasing temperature, resulting in lower currents at 60°C than at 23°C. Studying the adsorption, dehydrogenation and oxidation of methanol on Pt(111) in alkaline solution, Spendelow et al. identified CO as the main poisoning species, which affects methanol dehydrogenation rate as well as the CO oxidation as the main limiting step [68]. A study of the role of OH\textsubscript{ad} species and of the influence of anions in the methanol oxidation on a Pt electrode in different alkaline solutions (NaOH, Na\textsubscript{2}CO\textsubscript{3} and NaHCO\textsubscript{3}) revealed that adsorption of carbonate and bicarbonate on the electrode surface reduce the extent of OH adsorption and the activity of the electrode [69]. Comparable findings on the effect of carbonate / bicarbonate adsorption were reported by Tripkovic et al. [70].
Fig. 5.2 Recorded transients of the Faradaic current during potentiostatic oxidation of ethanol on different catalyst electrodes: (a) Pt/C catalyst, (b) PtRu black catalyst, (c) Pd/C catalyst and (d) Pd/CeO\(_2\)/C catalyst in 0.1 M ethanol + 0.5 M NaOH solutions. Temperatures see figure, electrolyte flow rate 15 \(\mu\)l s\(^{-1}\).

At 0.6 V and 0.7 V reaction potential, the temperature dependence of the steady-state ethanol oxidation currents reverts to a ‘normal’ Arrhenius behavior. In both cases, the current increases by a factor of \(~4\) when increasing the temperature from 23 to 90°C. The change in reaction behavior compared to the lower reaction potentials is related to differences in the nature and stability of the adlayer of adsorbed reaction intermediates /side products formed during reaction. The formation of such species is known to be potential dependent [21], with the incomplete oxidation product acetate prevailing at higher potential [17,22].

The current transient profiles measured on the PtRu black catalyst generally resemble those measured on the Pt/C catalyst, with the exception that the reaction times at each potential
were shorter (300 s) and that the different potentials were measured sequentially, stepping the potential to increasingly higher potential. The main characteristics can be summarized as follows: (i) the onset potential is at about 0.2 V, i.e., ~100 mV down-shifted compared with Pt/C. This is tentatively ascribed to the easier formation of OH\textsubscript{ad} on the Ru sites at low potential. (ii) The Faradaic current increases with increasing temperature at all potentials, different from the inverse behavior of the Pt/C catalyst at low potentials (0.4 and 0.5 V). iii) The increase depends significantly on the reaction potential. Furthermore, at 0.4 V and 0.5 V, the Faradaic current increases more steeply in the lower temperature range, from 23 to 60°C, than at higher temperatures, from 80 to 100°C (see also section 5.2.4). At 0.5 V, for example, it doubled for the temperature increase from 23 to 60°C, while it remains almost constant between 80 and 100°C (80°C: 0.25 mA, 100°C: 0.26 mA). This is tentatively attributed to increasing OH\textsubscript{ad} formation on the Ru sites and thus faster oxidation of CO\textsubscript{ad} or CH\textsubscript{x,ad} species to (bi)carbonate in the lower temperature regime, while at 80 and 100°C, excessive formation of OH\textsubscript{ad} increasingly hinders the dissociative adsorption/oxidation of ethanol and thus limits the current. (iv) Going from 0.6 V to 0.7 V, the Faradaic current decreases at all temperatures, again due to the increased oxide formation on the PtRu surface. (v) The absolute values of the Faradaic currents on the PtRu black film electrodes are significantly lower than those obtained on the Pt/C film electrodes, which we interpret in terms of a lower activity of the PtRu catalyst for dissociative adsorption of ethanol, due to the lower number of active Pt sites and/or due to an Ru induced reduced activity of the Pt sites for this process. The latter would fit to the reduced activity of the Pt surface atoms in PtRu surfaces well known from H\textsubscript{upd} and OH\textsubscript{ad} adsorption/desorption [71,72].

For the Pd/C catalyst, we found a measurable Faradaic current for all temperatures at 0.4 V (see inset in Fig. 5.2c). At potentials of 0.4 V and 0.5 V, the Faradaic current-time profiles reach a stable value within 8 s after the potential step at all temperatures, which is very different from the rapid initial decay observed for the Pt/C and PtRu catalysts. (Figs. 5.2a, 5.2b). Obviously, the Pd/C catalyst is less susceptible to poisoning by adsorbed reaction intermediates / side products, which agrees well with reports that acetate is the major reaction product on this catalyst [30,39,40,73,74]. This agrees also with a report that on a Pd/C catalyst less than 5% of the ethanol is converted to the complete oxidation product (carbonate) in 1.0 M KOH solution containing 1 M ethanol at room temperature [36]. At 0.6 V, the current
profiles resemble those at 0.5 V below 60°C, except for the higher absolute current values, while at higher temperatures (80 and 100°C), they exhibit an increasing deactivation tendency. The measurements at 100°C for 0.7 V are not included due to the extensive gas evolution at the counter electrode, which causes instabilities in the measured current and finally loss of the contact to the counter electrode.

For the Pd/CeO$_2$/C catalyst, we find a measurable Faradaic current increase with increasing temperature already at a potential of 0.2 V (see inset in Fig. 5.2d), similar to the PtRu black catalyst. The rapid build-up of stable current-time profiles at 0.3 and 0.4 V after the potential step indicates a high stability towards poisoning by strongly adsorbed species, either due to low C-C bond breaking rate, i.e., prevailing incomplete oxidation, or due to more facile removal of these adsorbates. At 0.5 V, the ethanol oxidation rate reaches a stable value simultaneously with the potential step at lower temperature (below 80°C) and decays slowly at higher temperatures. At 0.6 V, these characteristics are even more pronounced than at 0.5 V, with an even steeper increase and a faster decay in Faradaic current. Stepping the potential from 0.6 to 0.7 V at the respective temperature has little effect on the Faradaic current, it continues to decrease with time, continuing the decay observed at 0.6 V. This different characteristics of the Faradaic current changes when stepping the potential from 0.6 to 0.7 V compared to that of the Pd/C catalyst is possibly due to the abundance of oxygen-containing species on Pd/CeO$_2$/C catalyst.

Comparison between the Pt/C and PtRu black catalysts on the one hand and between the Pd/C and Pd/CeO$_2$/C catalysts on the other hand shows that the addition of the oxophilic component Ru to the Pt component and CeO$_2$ to the Pd/C catalyst increases the tolerance towards poisoning at lower potentials in the potentiostatic and potentiodynamic measurements. This can be explained by the ability of CeO$_2$ and Ru to supply oxygen-containing species at low potentials, which improves the oxidation of catalyst poisoning CO$_{ad}$ species. Similar as in acidic medium, acetaldehyde (in the form of diolate in alkaline medium), acetic acid (acetate ion in alkaline medium) and carbon dioxide ((bi)carbonate in alkaline environment) are considered as reaction products in the EOR in alkaline electrolyte, which are also detected by electrochemical methods combined with other techniques, such as HPLC [22] or in situ Fourier transform infrared spectroscopy (FTIR) [37,75]. Correspondingly, the severe
poisoning of the Pt/C catalyst can be ascribed to strongly adsorbed species such as CO$_{ad}$ or CH$_{x,ad}$ species. On the other hand, the higher activity of the Pd/C catalyst may be due to its lower poisoning, due to a lower ability for C-C bond dissociation, which results in incomplete oxidation of ethanol, mainly to acetate in alkaline solution [35,75-77]. This can also explain the different ratios of the peak currents in the positive- and negative-going scan mentioned above (see section 5.2.1): For the Pt/C catalyst, the stable adsorbed species, mainly CO$_{ad}$, will block active surface sites in the positive-going scan, but much less in the negative-going scan, while for the Pd/C catalyst, CO$_{ad}$ formation /oxidation is less pronounced [35,75].

Comparing the potential and temperature dependence of the Faradaic current for the different catalysts, we find the highest current for the Pt/C catalyst at 0.5 V at 23°C, while at 80°C a further potential increase still leads to increasing currents (maximum current at 0.7 V). For the Pd/C catalyst, the best performance was obtained at 0.7 V for both temperatures. For the PtRu black catalyst, the Faradaic current reaches its maximum value at 0.5 V and decreases at higher potentials of 0.6 and 0.7 V, also for both temperatures. Finally, the Pd/CeO$_2$/C catalyst reaches its maximum current at 0.6 V.

The main results of the potentiostatic EOR measurements on the respective catalysts, at different potentials, can be summarized as follows:

(i) In general, the steady-state Faradaic currents increase significantly with increasing temperature, with the exception of the Pt/C catalyst at 0.4 and 0.5 V, where the current decreases from 23 to 80°C, and remains about constant at 90°C. The significant difference between the Pt/C and Pd/C catalyst performance is explained by an enhanced formation of reaction inhibiting adsorbates such as CO$_{ad}$ or CH$_{x,ad}$ species on the Pt/C catalyst under these conditions, due to a higher C-C bond breaking activity, which overcompensates the simultaneous increase in adsorbate oxidation rate, while this is not the case on the other catalysts.

(ii) The addition of the oxophilic components Ru (to Pt/C) and CeO$_2$ (to Pd/C) improved the tolerance towards poisoning at lower potential and the stability towards deactivation, but did not promote the activity at typical operation potential ($\geq$ 0.4 V). Thermal activation leads to an increase of the Faradaic current by factors of $\sim$3 at 0.4 V and 2.5 at 0.5 V for the PtRu
black catalyst, by factors of ~6 at 0.4 V and 7 at 0.5 V for the Pd/CeO$_2$/C catalyst with increasing temperature (23 → 80°C).

(iii) The tolerance towards poisoning depends on the potential. Under present reaction conditions, it decreases in the following order: Pd/CeO$_2$/C > Pd/C > PtRu black > Pt/C at lower potential (0.4 V and 0.5 V), but Pd/CeO$_2$/C > PtRu black > Pd/C > Pt/C at high potential (0.7 V).

(iv) Comparison of the Faradaic current at 0.6 and 0.7 V at the same temperatures, but different electrodes, reveals characteristic differences between the monometallic catalysts (Pt/C and Pd/C catalyst), where the current increases from 0.6 to 0.7 V at all temperatures, and the bimetallic/two component catalysts (PtRu black and Pd/CeO$_2$/C catalyst), where the current decreases. This decrease is attributed to the enhanced OH adsorption/oxide formation.

In total, the temperature and potential dependent behavior indicates an increasing activation of the EOR on both Pt-based and Pd-based catalysts with temperature, the differences in the ethanol oxidation reaction characteristics on Pt-based catalyst versus Pd-based are mainly attributed to differences in the activity for C-C bond breaking and the resulting formation/removal of reaction inhibiting adsorbates.

### 5.2.3 Mass specific currents and active surface area specific current densities

In order to exclude the influence of metal loading and the electrochemical active surface areas of the respective catalysts on the ethanol oxidation activity, the steady-state Faradaic currents in Fig. 5.2 were converted into metal mass specific currents (Figs. 5.3a and 5.3b) and active surface area specific current densities (Figs. 5.3c and 5.3d). The electrochemical active surface areas were determined by CO$_{\text{ad}}$ stripping at 23°C (see corresponding CO stripping information in Chapter 2). The values resulting for 23°C (upper panels) and 80°C (lower panels) are presented in Fig. 5.3, a complete compilation of the values is given in Table 5.1. The activities at low potentials (0.2 and 0.3 V) are also shown in larger magnification for better identification.

For the technically-relevant metal mass specific activities, measurable currents were detected at the lowest potential of 0.2 V on the PtRu black and Pd/CeO$_2$/C catalysts, both at 23°C and 80°C (see insets in Figs. 5.3a, 5.3b), with the latter showing a higher mass specific
activity (23°C: 0.2 µA µg\(^{-1}\) for PtRu black vs. 0.6 µA µg\(^{-1}\) for Pd/CeO\(_2\)/C, 80°C: 1.1 µA µg\(^{-1}\) vs. 2.4 µA µg\(^{-1}\)). At 0.3 V, both mass specific activities increase (8 µA µg\(^{-1}\) vs. 10 µA µg\(^{-1}\)) as compared to those at 0.2 V. As mentioned before, the lower increase in activity on the Pd/CeO\(_2\)/C catalyst is associated with surface blocking by an increasing excess of oxygen containing species on that catalyst at higher temperature (80°C), resulting in a decrease of the number of active sites for dissociative adsorption of ethanol molecules. This is also in agreement with recent findings that CeO\(_2\) can not adsorb and oxidize CO\(_{ad}\), but only provides oxygen-containing species for CO\(_{ad}\) oxidation at low potential, while on Pt hydroxyl groups are produced at higher potentials [78].

**Fig. 5.3** Specific activity (mA/mg) during potentiostatic oxidation of ethanol of the different catalysts: Pt/C catalyst (10 µg\textsubscript{Pt} cm\(^{-2}\)), PtRu black catalyst (66 µg\textsubscript{Pt} cm\(^{-2}\)), Pd/C catalyst (40 µg\textsubscript{Pd} cm\(^{-2}\)) and Pd/CeO\(_2\)/C catalyst (40 µg\textsubscript{Pd} cm\(^{-2}\)) (see figure) in 0.1 M ethanol + 0.5 M NaOH solutions at 23°C (upper panel) and 80°C (lower panel). Electrolyte flow rate 15 µl s\(^{-1}\).

**Table 5.1** Mass specific currents and active surface area specific current densities in the EOR for the different catalysts at different potentials, determined from steady-state reaction currents in Fig. 5.2.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T / °C</th>
<th>Reaction potential / $V_{RHE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>$I / mA$</td>
<td>$I / mA$</td>
</tr>
<tr>
<td>Pt/C</td>
<td>23</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>–</td>
</tr>
<tr>
<td>PtRu</td>
<td>23</td>
<td>0.0002</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.0011</td>
</tr>
<tr>
<td>Pd/C</td>
<td>23</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>–</td>
</tr>
<tr>
<td>Pd/CeO$_2$/C</td>
<td>23</td>
<td>0.0006</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.0024</td>
</tr>
</tbody>
</table>
At 0.4 V, the mass specific activity decreases in the order Pt/C > Pd/\text{CeO}_2/C > \text{PtRu black} > Pd/C at 23°C, while at 80°C this order has changed to Pd/\text{CeO}_2/C > \text{PtRu black} > Pt/C > Pd/C. The unusual temperature dependence of the Pt/C catalyst, with a current decrease with increasing temperature, is of course observed also in the mass specific currents, while for the other catalysts the mass specific current increases, by a factor of 4 for the PtRu black catalyst, 3 for the Pd/C catalyst and 6 for the Pd/\text{CeO}_2/C catalyst. As mentioned before, the significant difference indicates that the addition of Ru or CeO\textsubscript{2} will promote the poisoning tolerance towards CO\textsubscript{ad} or CH\textsubscript{x,ad} species. At 23°C, the mass specific current density is highest on the Pt/C catalyst up to 0.6V, and only at 0.7V the Pd/C catalysts performs better, by almost a factor of 3. In contrast, at 80°C, the Pd/C catalyst shows the highest mass specific activity already at 0.5 V, and at 0.7 V it is more than a factor of 2 better than that of the Pt/C catalyst. Hence, at technically relevant conditions (continuous electrolyte flow, constant potential, elevated temperature), the Pd/C catalyst shows the highest activity at potentials ≥0.5 V. Only at lower potentials (0.2 – 0.4 V), other catalysts perform better under these conditions. At 0.5 V, however, the difference between Pd/C and Pd/\text{CeO}_2/C catalysts is small. These results clearly point to an improved performance of the Pd/C catalyst compared to the Pt/C catalyst under technically relevant conditions, only at low potentials (≤0.4 V) addition of CeO\textsubscript{2} as oxophilic co-catalyst results in further improvement.

The intrinsic active surface area normalized activities (active surface area normalized current densities, Figs. 5.3c, 5.3d) show slightly different characteristics as compared to the mass specific activities, which reflects the differences in active surface area of the different catalysts. Compared to the trends in metal mass specific currents, the main differences are i) the even more distinct difference in activity between Pd/C and Pt/C catalysts, with the former one showing a better performance at ≥0.6 V at 23°C and at ≥0.4 V at 80°C and ii) the somewhat higher activity of the ‘bimetallic’ PtRu black and Pd/\text{CeO}_2/C catalyst. At low potentials, at ≤0.4 V at 23 and at 80°C, respectively, they show the highest activity, underlining the role of the oxophilic second component at low potentials.
5.2.4 Apparent activation energies

The apparent activation energies $E_a$ for the ethanol oxidation reaction, determined from temperature dependent steady-state Faradaic currents at the respective reaction potentials, were calculated from the Arrhenius plots shown in Fig. 5.4. The resulting values are listed in Table 5.2. For the Pt/C catalyst, which showed a decrease of the Faradaic current with temperature at 0.4 and 0.5 V, we used the initial maximum currents at these potentials, after correction for double-layer charging, to obtain activation energies reflecting the inherent activities rather than the blocking by stable adsorbates (see below).

The plots of the logarithmic oxidation rates vs. $1/T$ in Fig. 5.4 generally show a linear dependence, perhaps with the exception of the Pt/C catalyst, where the highest temperature values (90°C) seems to deviate at all potentials. This implies that, except perhaps for Pt/C, the rate determining step does not change over the entire temperatures range.

![Arrhenius plots](image)

**Fig. 5.4** Arrhenius plots of the steady-state ethanol oxidation rate in 0.1 M ethanol + 0.5 M NaOH solution at different potentials (potentials see figure) on different catalyst electrodes: (a) Pt/C catalyst (after 15 min), (b) PtRu black catalyst, (c) Pd/C catalyst, and (d) Pd/CeO$_2$/C catalyst. Electrolyte flow rate 15 µl s$^{-1}$, Faradaic currents measured after about 300 s, if not mentioned otherwise.
The apparent activation energies of the EOR on the Pt/C catalyst electrode, as determined from the steady-state Faradaic current, are 15±4 kJ mol\(^{-1}\) and 20±1 kJ mol\(^{-1}\) at 0.6 V and 0.7 V, respectively (see Table 5.2). As mentioned in Chapter 2, at 0.4 and 0.5 V, the steady-state Faradaic currents decrease on this catalyst with increasing temperature up to 80°C, which is equivalent to a negative activation energy. This was attributed to an increasing blocking of the surface by stable adsorbates, rather than to a negative barrier in an elemental reaction step (see section 5.2.2). In order to assess the inherent activity of the material, we evaluated the temperature dependent initial currents (initial current maxima), after correction for double-layer charging (see Fig. 5.4a). The resulting currents yield values for \(E_a\) of 26±4 kJ mol\(^{-1}\) at 0.4 V and 32±4 kJ mol\(^{-1}\) at 0.5 V, respectively, which fit well to the data obtained at higher potentials (see Table 5.2). Because of the different schemes for evaluation, however, quantitative considerations of the potential dependence are hardly possible for this catalyst. For the PtRu black catalyst, the values for \(E_a\) first decay continuously with potential, from 30±1 kJ mol\(^{-1}\) at 0.2 V via 28±3 kJ mol\(^{-1}\) at 0.3 V and 15±3 kJ mol\(^{-1}\) at 0.4 V to the minimum value of 11±2 kJ mol\(^{-1}\) at 0.5 V; with further increasing potential, \(E_a\) increases to 14±1 kJ mol\(^{-1}\) at 0.6 V and 20±6 kJ mol\(^{-1}\) at 0.7 V.

### Table 5.2 Apparent activation energies for ethanol oxidation at different potentials, determined from steady-state reaction currents (see Fig. 5.4).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 V</td>
</tr>
<tr>
<td>Pt/C</td>
<td>–</td>
</tr>
<tr>
<td>PtRu black</td>
<td>30 ± 1</td>
</tr>
<tr>
<td>Pd/C</td>
<td>–</td>
</tr>
<tr>
<td>Pd/CeO(_2)/C</td>
<td>21 ± 3</td>
</tr>
</tbody>
</table>
These data can be compared with results obtained for related systems under comparable reaction conditions. Jiang et al. reported apparent activation energies for the EOR on a Pt/C catalyst in the range of 25 to 42 kJ mol\(^{-1}\) in 0.1 M NaOH solution containing 0.01 M ethanol (temperature range: 22, 40 and 60°C, potential range 0.4 to 0.6 V\(_{\text{RHE}}\)) based on both potentiodynamic and potentiostatic measurements [20].

Investigating the EOR kinetics on Pt/C and PtPdAu/C catalysts in the temperature range of 20–80°C in 0.5 M NaOH containing 1.0 M ethanol by potentiostatic measurements, Datta et al. obtained apparent activation energies on the Pt/C catalyst in the range of 9.0–3.6 kJ mol\(^{-1}\) at reaction potentials between 0.52 and 1.12 V (−0.4 and 0.2 V vs. Hg-HgO) [76]. It should be noted that the values of the apparent activation energies for ethanol oxidation on the Pt/C catalyst are significantly lower in alkaline electrolyte than in acidic environment [41]. Under otherwise similar reaction condition, we obtained \(E_a\) values of 41 ± 2 kJ mol\(^{-1}\) and 40 ± 2 kJ mol\(^{-1}\) at potentials of 0.58 and 0.68 V, respectively, in 0.1 M ethanol solution containing 0.5 M H\(_2\)SO\(_4\), compared to 15±4 kJ mol\(^{-1}\) and 20±1 kJ mol\(^{-1}\) at 0.6 V and 0.7 V under present conditions. At 0.6 V, oxidative removal of CO\(_{\text{ad}}\) is facile on the Pt/C catalyst due to sufficient formation of adsorbed hydroxyl species, and at 0.7 V, CO\(_{\text{ad}}\) oxidation is very fast. Under these conditions, C-C bond rupture becomes rate limiting, and the resulting \(E_a\) should correspond to the activation barrier for this step at 0.7 V.

Similar trends for the activation energy were reported also for methanol oxidation on Pt/C catalysts in alkaline electrolyte. Cohen et al. [58] determined apparent activation energies for methanol oxidation on polycrystalline Pt electrode in the range between 16 and 39 kJ mol\(^{-1}\), depending on the reaction potential. These data were obtained from the anodic sweep data in potentiodynamic measurement in 0.1 M KOH containing 0.5 M methanol solution. The apparent activation energies first decrease with potential, reaching a minimum value at about 0.8 V\(_{\text{RHE}}\) (−0.125 V vs. Ag/AgCl) and then increases again with higher potentials, where oxide formation replaces OH\(^{-}\) adsorption [58].

For reaction on PtRu black, the abundance of OH\(_{\text{ad}}\) species on Ru sites facilitates the oxidative removal of dissociated adsorbate species or promotes the incomplete oxidation of ethanol / acetaldehyde to acetate at the lower potential of 0.2 and 0.3 V.
For the Pd/C catalyst electrodes, $E_a$ first increases with potential, from 24±3 kJ mol$^{-1}$ at 0.4 V to 29±3 kJ mol$^{-1}$ at 0.5 V, and then decreases to 24±3 kJ mol$^{-1}$ at 0.6 V and 17±1 kJ mol$^{-1}$ at 0.7 V. Finally, for the Pd/CeO$_2$/C catalyst, the tendency of the $E_a$ values is similar to that of the PtRu black catalyst with $E_a$ first increasing from 21±3 kJ mol$^{-1}$ at 0.2 V to 28±4 kJ mol$^{-1}$ at 0.3 V and 32±3 kJ mol$^{-1}$ at 0.4 V, and then decreasing to 30±1 kJ mol$^{-1}$ at 0.5 V, 24±2 kJ mol$^{-1}$ at 0.6 V and 24±1 at 0.7 V. The lower value at 0.2 V for the Pd/CeO$_2$/C catalyst as compare to the PtRu black catalyst (30±1 kJ mol$^{-1}$) may be rationalized by a facile supply of oxygen species CeO$_2$ with its high capacity for storing/releasing oxygen or due to an easier formation of oxygen containing species on ceria, comparable to the role of Ru in PtRu, which facilitates oxidation of adsorbed species accumulating on the Pd catalyst at low potentials [27,30,31,33,40,55,78,79].

The increase of $E_a$ increase with increasing potential, to ~30 kJ mol$^{-1}$ at 0.5 V, is likely to increasingly reflect the characteristics of C-C bond rupture on Pd, which becomes rate limiting due to the sufficient supply of oxygen containing species. At higher potentials, 0.6 and 0.7 V, oxide formation on the surface promotes the process for incomplete oxidation of ethanol to acetate, corresponding to a decrease of $E_a$ as deduced from the EOR selectivity at this potential in acidic medium [41]. Similar values were also reported by Wang et al. in a study on the electrooxidation of methanol, ethanol and 1-propanol on a Pd electrode in 1.0 M KOH solution containing 1.0 M ethanol using linear sweep voltammetry (LSV) with a sweep rate of 5 mV s$^{-1}$, where they obtained a value of 26.3 kJmol$^{-1}$ for the apparent activation energy at about 0.65 V$_{RHE}$ (-0.4 V vs. SCE) (temperature range of 10 - 50°C), which agrees well with our result at 0.6 V [80].

For practical applications, the lower values of the apparent activation energy (in the range of 11 ~ 32 kJ mol$^{-1}$) indicate, that the increase in activity accessible by a further increase in temperature will only be slow, significantly slower than for reaction in acidic environment.

5.3 Conclusions

The ethanol electrooxidation was studied by potentiodynamic and potentiostatic measurements on different Pt-based (Pt/C and PtRu black) and Pd-based (Pd/C and
Pd/\text{CeO}_2/C)\) thin-film catalyst electrodes under well-defined reaction and transport conditions, such as controlled electrolyte transport, continuous reaction and elevated temperature and pressure, led to the following conclusions:

1. The activities for ethanol electrooxidation, as given by the steady-state currents, increases with increasing reaction temperature for the different electrodes investigated. Only for the Pt/C catalyst at 0.4 and 0.5 V, the steady-state Faradaic currents first decrease with increasing temperature from 23 to 80°C followed by an increase above 80°C.

2. The addition of Ru component to Pt as well as CeO\textsubscript{2} to Pd/C facilitate the onset of ethanol oxidation reaction at lower potential and increasing reaction temperature further promote the negative-shift of onset potentials to low values for respective electrode.

3. The difference in the ratio of peak currents in negative-going scans vs. positive-going scans between Pt-based catalyst (below 1) and Pd-based electrodes (above 1) points to distinct differences in the potential dependent coverage of adsorbate species and in the influence of these adsorbed species on the reaction process.

4. The comparison of mass specific and active surface area normalized activities for ethanol oxidation reaction between the respective electrode at 80°C and at 23°C shows different characteristics: the best mass and active surface area specific activities are obtained on the Pd/C catalyst at high potential of 0.7 V at both temperature (23 and 80°C); for Pt/C catalyst, the better activities are obtained at 0.5 V (23°C) and 0.7 V (80°C), respectively. At higher potentials, better mass / active surface area specific activities are obtained on the mono-metallic catalyst (Pt/C > PtRu black and Pd/C > Pd/\text{CeO}_2/C).

5. The linear correlation between ln i and 1/T in the corresponding Arrhenius plots on Pt-based and Pd-based catalyst indicates that the rate limiting steps do not change in the entire reaction temperature range, with the possible exception of the Pt catalyst, resulting in values of the apparent activation energy in the range of 11 - 32 kJ mol\textsuperscript{-1}.

Finally, the temperature dependent behavior of ethanol electrooxidation on different electrodes involved in the present study emphasizes the importance of fuel cell relevant reaction and mass transport conditions in model studies on fuel cell reactions.
Acknowledgements

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References


Chapter 6

Summary
6.1 Summary (English version)

The goal of this research was to determine the kinetics of the electrooxidation of small organic molecules (C₂ molecules), in terms of the activity (Faradaic current) and selectivity (current efficiency for CO₂ formation) on realistic carbon supported Pt/Vulcan and related electrocatalysts under well-defined, but nevertheless, fuel cell relevant reaction conditions (elevated temperatures up to 100 °C, an overpressure of 3 bar and continuous mass transport). The results are important for further design and optimization of catalysts aiming at improvement of performance and durability relevant for direct ethanol fuel cells (DEFC).

Systematic kinetic measurements were performed in a novel high temperature / high pressure thin-layer electrochemical flow cell, which allowed a combination of on-line differential electrochemical mass spectrometry (DEMS) for monitoring CO₂ (m/z = 44) formation (reflecting the rate for C-C bond breaking) and simultaneous electrochemical measurements, such as cyclic voltammetry and chronoamperometry. This way, the resulting current efficiency for CO₂ formation (fuel utilization) could be determined as a function of temperature, electrode potential and catalyst composition, as well as apparent activation energy at different potentials, over various catalysts and reaction conditions (acidic or alkaline medium).

Model studies for ethanol electrooxidation on a thin-film Pt/Vulcan catalyst electrode (ca. 100% catalyst utilization, negligible diffusion limitations) in 0.5 M H₂SO₄ solution are presented in Chapter 3, aiming to elucidate the influence of temperature, potential and concentration on the reaction activity and selectivity. Similar measurements on the electrooxidation of acetaldehyde and acetic acid are presented in chapter 4.

The measurements reveal a pronounced temperature effect on the ethanol (Chapter 3) / acetaldehyde (Chapter 4) electrooxidation, with a negative-going shift of the onset potential to lower values for both Faradaic current and mass spectrometric current with increasing temperature. This is related to the thermal activation of the ethanol / acetaldehyde adsorbate oxidation and of the OH_ads formation. Both the overall reaction rate (I_F) and the rate for CO₂ formation (I_MS(m/z = 44)) increase significantly with temperature, the resulting current efficiency for CO₂ formation increases from 5% at 23 °C to ~87% at 100 °C (both obtained at 0.48 V in 0.01 M ethanol solution). This indicates an increasing role of thermal activation for
the C-C bond cleavage (CO₂ formation). A similar temperature effect was also found in the electrooxidation of acetaldehyde (Chapter 4), which is also one of the main byproducts (another one is acetic acid) in the ethanol electrooxidation reaction, under the same reaction conditions. In this case, the CO₂ current efficiency for acetaldehyde electrooxidation varied from 9% at 23 °C to ~41% at 100 °C (acquired at 0.6 V in 0.01 M acetaldehyde solution).

The influence of the electrode potential on the reaction activity and selectivity (presented in Chapter 3 and Chapter 4) and the resulting potential-dependent variation of the CO₂ current efficiency confirm that both the overall (I_F) and partial reaction rate (CO₂ formation rate) are controlled by the potential-dependent composition and the coverage of the adlayer. The coverage of adsorbed C₁ species resulting from dissociative adsorption of the model molecules (such as ethanol, acetaldehyde) is higher at lower potential, resulting in an inhibiting layer for the oxidation onset (I_F and I_MS are suppressed at this low potential region). Shifting the applied potential to higher values, the coverage of CO_ad decreases due to CO_ad oxidation governed by OH_ad formation. At even higher potential, the coverage of CO_ad decreases due to more efficient CO_ad oxidation and a decreasing CO_ad formation (C-C bond dissociation) rate on the oxy-species covered surface. Here an increasing coverage of OH_ad / surface oxide species have a negative effect by reducing the number of pairs of vacant surface sites required for the C-C bond breaking. These potential-dependent characteristics are also verified by the potential-dependent current efficiencies for CO₂ formation during ethanol / acetaldehyde electrooxidation reaction, where the CO₂ current efficiencies decrease from 87% (0.48 V) to 17% (0.68 V) for ethanol oxidation reaction (Chapter 3) and from 41% (0.6 V) to 17% (0.7 V) for acetaldehyde oxidation reaction (Chapter 4), both from 0.01 M model molecule solution.

This is further correlated to variations of the potential-dependent apparent activation energies found from the Arrhenius plots for the overall reaction rate and for the CO₂ formation in the entire temperature range studied (Chapter 3-4), whose linearity qualitative suggests that the reaction rate determining step (r.d.s.) does not change in this temperature range. The change in the slope of the Arrhenius plots with the potential results in different values of the apparent activation energies, where the rate determining step (r.d.s.) is related to CO_ad oxidation at lower potentials, whereas the r.d.s. is connected to the C-C bonding breaking (CO_ad formation) at high potentials with a higher value of apparent activation energies. A method for
estimating the temperature for the complete conversion of model molecules (ethanol, acetaldehyde) to CO$_2$ formation is proposed by extrapolating the Arrhenius plots for the overall (Faradaic) and the partial current for CO$_2$ formation up to their intercept, which yields 100% current efficiency for CO$_2$ formation (Chapter 3-4) at ~175 °C (at about 0.6 V and 0.1 M ethanol solution) for ethanol oxidation and about 364 °C (at 0.6 V and 0.1 M acetaldehyde solution) for acetaldehyde electrooxidation. This method allows to predict in model studies the temperature for a complete conversion of the organic fuel to CO$_2$, which is important for practical fuel cell systems.

As underlined throughout the present work, a well-defined mass transport is an essential prerequisite for the quantitative interpretation of the kinetic characterists because of its significant influence on the overall reaction rate (activity) and the corresponding product distribution (selectivity). Concentration-dependent model studies on ethanol and acetaldehyde oxidation reactions under controlled mass transport are presented in Chapters 3-4 as a function of the electrode potential and the reaction temperature. Here the importance of the improvement of the experimental set-up for minimizing the evaporation of acetaldehyde and thus maintaining the losses of concentration of acetaldehyde at elevated temperatures at a tolerable level should be noted. For ethanol oxidation, the corresponding current efficiencies for CO$_2$ formation decrease with increasing ethanol concentration, which can be reasonably explained by the transport effects within the “desorption-re-adsorption-further reaction” concept (details see section 1.3.2 and 3.2.2 and the references cited therein). According to that concept a reactive product of incomplete ethanol oxidation - e.g., acetaldehyde (with the assumption that ethanol oxidation will produce three main products, namely, acetaldehyde, acetic acid and CO$_2$) - can re-adsorb and react further to CO$_2$ before leaving the diffusion layer, which is also well known in heterogeneous catalysis where a lower space velocity is known to drive the product distribution towards their equilibrium composition. This agrees with the variation of the current efficiencies for CO$_2$ formation from 26% in 0.1 M ethanol solution to 32% in 0.01 M ethanol solution (both at 0.6 V and 100 °C). Contributions of re-adsorption of incomplete oxidation products can be excluded in acetaldehyde oxidation (Chapter 4), because its only incomplete oxidation product, acetic acid, does not react further at present reaction conditions, as shown by the much lower reaction rate for acetic acid electrooxidation reaction even at elevated temperatures (Chapter 4).
Besides the influence of the experimental parameters mentioned above, such as temperature, potential and concentration on the activity and the corresponding selectivity, the pH will also influence on the ethanol electrooxidation activity. This is illustrated in Chapter 5 for the ethanol oxidation reaction in alkaline solution on different electrodes, where the temperature and potential effect played an important role in the corresponding activities. The steady-state Faradaic current increases with increasing temperature on all electrodes except that on Pt/C catalyst at 0.4 and 0.5 V, where the corresponding steady-state currents first decreased with temperature (below 80 °C), followed by an increase above 80 °C. The addition of Ru to Pt or of CeO$_2$ to the Pd/C catalyst results in a negative shift in the onset potential and can be further promoted by increasing temperature with a further negative shift in onset potential. The linear slope of the logarithmic oxidation rates with 1/T observed on all electrodes indicates that the rate determining step is the same over the entire temperature range. It results in values of the apparent activation energy in the range of 11 - 32 kJ mol$^{-1}$. The different values of the apparent activation energies for the respective electrodes are mainly attributed to variations in the adsorbate layer, which also affect the electrochemically active surface area specific and mass specific activities. The highest mass and active surface area specific activities are obtained on the Pd/C catalyst at high potential of 0.7 V at both temperature (23 and 80 °C); for the Pt/C catalyst, the highest activities are obtained at 0.5 V (23 °C) and 0.7 V (80 °C), respectively. At higher potentials, better mass / active surface area specific activities are obtained on the mono-metallic catalyst (Pt/C > PtRu black and Pd/C > Pd/CeO$_2$/C).

The temperature, potential, concentration, pH effects determined in the present work, which are illustrated in differences in the activity, selectivity (CO$_2$ current efficiency), and the potential dependent variations (concentration also plays a role) of the apparent activation energies illustrate that the mechanism for ethanol oxidation proceeds via a complex network of individual reactions, where the overall activity ($I_F$) only probes / represents the sum of all partial reaction activities. Similarly, the variation in the potential dependent apparent activation energies may be due to differences in the contributions from various reaction pathways.

Summarizing the systematic information on ethanol, acetaldehyde and acetic acid oxidation activity and selectivity gained from our HT/HP flow cell measurements in combination with DEMS, the model studies under realistic conditions can provide important information
relevant for practical direct ethanol fuel cell operation. First, increasing reaction temperatures not only result in a higher reaction rate, but also decrease the acetic acid formation. This is correlated to a higher activation barrier for complete oxidation of model molecules to CO$_2$ (vs. the overall apparent barrier). Actually, this also illustrated a requirement for improving the performance of the catalyst by selectively oxidizing acetaldehyde to CO$_2$, thus avoiding acetic acid formation, which can not be further oxidized (a reaction dead-end). Second, the possible improvements in the anode electrocatalysts do not only mean the activation for C-C bond breaking, but also need the capability for oxidative removal of the resulting adsorbed fragments to CO$_2$. This means only if the removal of these species is not rate limiting, a further increase of the C-C bond cleavage can lead to an overall improvement of the reaction kinetics (higher oxidation current). The ethanol electrochemical oxidation measurements in alkaline solution were performed in present work up to the 100 °C temperature, which exceeds the temperature stability range of anionic membranes, thus allowing to gain kinetic information over a wider temperature range.
6.2 Zusammenfassung

Ziel der Untersuchungen war es, die Kinetik der Elektrooxidation kleiner organischer Moleküle (C₂ Moleküle) im Sinne von Aktivität (Faraday’scher Strom) und Selektivität (Stromanteil der CO₂ Bildung) auf realistischen kohlenstoffgetragenen Pt/Vulcan und Katalysatoren unter wohldefinierten, aber trotzdem brennstoffzellenrelevanten Reaktionsbedingungen (erhöhte Temperaturen bis 100 °C, 3 bar Überdruck und kontinuierlicher Massentransport) zu bestimmen. Die Ergebnisse sind wichtig für das zukünftige Design und die Optimierung der Katalysatoren, was auf die Verbesserung der Leistung und der Haltbarkeit von Direktethanolbrennstoffzellen (direct ethanol fuel cells, DEFC) abzielt.

Die systematischen kinetischen Messungen wurden in einer neuen elektrochemischen Hochtemperatur/Hochdruck Dünnschichtflusszelle durchgeführt, die es ermöglichte, Messungen des elektrochemischen Stroms und online massenspektrometrische Messungen mittels Differentieller Elektrochemischer Massenspektrometrie (DEMS), in wie Zyklovoltammetrie und Chronoamperometrie zu kombinieren. Damit kann auch die CO₂ Bildung (m/z = 44), die ein Maß für die Geschwindigkeit der C-C Bindungsspaltung darstellt, verfolgt werden. Somit konnten der Stromanteil der CO₂ Bildung (Totaloxidation = vollständige Ausnutzung des Brennstoffs) in Abhängigkeit von der Temperatur, dem Elektrodenpotential und der Katalysatorzusammensetzung sowie die scheinbare Aktivierungsenergie bei verschiedenen Potentialen, auf unterschiedlichen Katalysatoren und unter verschiedenen Reaktionsbedingungen (saures oder alkalisches Medium) bestimmt werden.

Modelluntersuchungen zur Ethanoelektrooxidation auf Dünnfilm Pt/Vulcan Elektroden (ca. 100% Katalysatorausnutzung, vernachlässigbare Diffusionslimitierung) in 0.5 M H₂SO₄ Lösung, die darauf abzielen, den Einfluss von Temperatur, Potential und Konzentration auf die Aktivität und Selektivität der Reaktion aufzuklären, sind in Kapitel 3 dargestellt. Gleichartige Messungen zur Elektrooxidation von Acetaldehyd und Essigsäure sind in Kapitel 4 dargestellt.
Die Messungen zeigen einen deutlichen Einfluss der Temperatur auf die Elektrooxidation von Ethanol (Kapitel 3) und Acetaldehyd (Kapitel 4), wobei sich das Potential, bei dem sowohl der Faraday’sche als auch der massenspektrometrische Strom einsetzen, mit steigender Temperatur zu tieferen Werten verschiebt. Dies hängt mit der thermischen Aktivierung der Oxidation der Ethanol/Acetaldehyd-Adsorbate und der OH$_{ad}$ Bildung zusammen. Sowohl die Gesamtreaktionsgeschwindigkeit (I$_F$) als auch die CO$_2$ Bildungsrate (I$_{MS}(m/z = 44)$) steigen deutlich mit der Temperatur, wobei der resultierende Stromanteil der CO$_2$ Bildung von 5% bei 23 °C auf ~87% bei 100 °C steigt (beide Werte wurden bei 0.48 V in 0.01 M Ethanol Lösung erhalten). Dies weist auf eine zunehmende Bedeutung der thermischen Aktivierung für die C-C Bindungsspaltung (CO$_2$ Bildung) hin. Unter denselben Reaktionsbedingungen wurde ein ähnlicher Temperatureinfluss auch bei der Elektrooxidation von Acetaldehyd (Kapitel 4), das eines der wichtigsten Nebenprodukte (ein weiteres ist Essigsäure) der Ethanolelektrooxidation ist, gefunden. In diesem Fall varierte der Stromanteil der CO$_2$ Bildung bei der Acetaldehydelektrooxidation zwischen 9% bei 23 °C und ~41% bei 100 °C (gemessen bei 0,6 V in 0,01 M Acetaldehyd Lösung).

Der Einfluss des Elektrodenpotentials auf die Aktivität und Selektivität der Reaktion (in Kapitel 3 und Kapitel 4 dargestellt) und die resultierende potentialabhängige Änderung des CO$_2$ Stromanteils bestätigen, dass sowohl die gesamte (I$_F$) als auch die partielle Reaktionsrate (CO$_2$ Bildungsraten) von der potentialabhängigen Zusammensetzung und Bedeckung der Adsorbatschicht bestimmt werden. Die Bedeckung mit C$_1$ Adsorbaten, die sich aus der dissoziativen Adsorption der betreffenden Moleküle (Ethanol, Acetaldehyd) ergibt, ist bei tiefen Potentialen höher, was zu einer Adsorbschicht führt, die das Einsetzen der Oxidation verhindert (I$_F$ und I$_{MS}$ werden in diesem tiefen Potentialbereich unterdrückt). Wird ein höheres Potential angelegt, sinkt die CO$_{ad}$ Bedeckung aufgrund der CO$_{ad}$ Oxidation, die durch die OH$_{ad}$ Bildung bestimmt wird. Bei noch höherem Potential sinkt die CO$_{ad}$ Bedeckung wegen gesteigerter CO$_{ad}$ Oxidation und sinkender CO$_{ad}$ Bildungsraten (Rate der C-C Bindungsspaltung) auf der Oxid/Hydroxid bedeckten Oberfläche. Hier hat die steigende Bedeckung mit Oberflächen Oxid/Hydroxid einen negativen Einfluss, indem sie die Zahl der benachbarten Paare freier Oberflächenplätze verringert, die für die Spaltung der C-C Bindung benötigt werden. Diese potentialabhängige Charakteristik wird auch durch den potentialabhängigen CO$_2$ Stromanteil während der Ethanol-/Acetaldehyd Elektrooxidation
bestätigt, wo der CO\(_2\) Stromanteil von 87% (0,48 V) auf 17% (0,68 V) bei der Ethanoloxidation (Kapitel 3) und von 41% (0,6 V) auf 17% (0,7 V) bei der Acetaldehydoxidation (Kapitel 4), jeweils in 0,01 M Lösung des betreffenden Moleküls, abnimmt.

Zudem korreliert dies mit den potentialabhängigen, scheinbaren Aktivierungsenergien, die über die Arrhenius-Auftragungen im gesamten untersuchten Temperaturbereich (Kapitel 3-4) für die Gesamtreaktionsrate und die CO\(_2\) Bildung bestimmt wurden, wobei die Linearität der Auftragungen qualitativ darauf hindeutet, dass sich der Geschwindigkeitsbestimmende Schritt (rate determining step, r.d.s.) in diesem Temperaturbereich nicht ändert. Die Änderungen der Steigung der Arrhenius-Auftragungen mit dem Potential führen zu unterschiedlichen Werten der scheinbaren Aktivierungsenergie, wobei bei tiefen Potentialen die CO\(_{ad}\) Oxidation den r.d.s. darstellt, während bei hohen Potentialen der C-C Bindungsbruch (CO\(_{ad}\) Bildung), mit höheren Werten der scheinbaren Aktivierungsenergie, geschwindigkeitsbestimmend ist. Eine Methode, um die Temperatur für die vollständige Oxidation der Modellmoleküle (Ethanol, Acetaldehyd) zu CO\(_2\) abzuschätzen besteht darin, die Arrhenius-Auftragungen für den Faraday'schen Strom und den partiellen Strom der CO\(_2\) Bildung bis zu ihrem Schnittpunkt zu extrapolieren, was einen Stromanteil der CO\(_2\) Bildung von 100% bei ~175 °C (bei ca. 0,6 V und 0,1 M Ethanol Lösung) für die Ethanoloxidation und ungefähr 364 °C (bei 0,6 V und 0,1 M Acetaldehyd Lösung) für die Acetaldehydelektrooxidation ergibt. Diese Methode erlaubt es, die Temperatur für die vollständige Umsetzung des organischen Brennstoßs zu CO\(_2\) mit Modelluntersuchungen vorherzusagen, was wichtig für praktische Brennstoffzellensysteme ist.

Wie in vorliegender Arbeit unterstrichen wurde, ist ein wohldefinierter Massentransport für die quantitative Interpretation der kinetischen Charakteristik von essentieller Bedeutung, da er einen signifikanten Einfluss auf die Gesamtreaktionsgeschwindigkeit (Aktivität) und die entsprechende Produktverteilung (Selektivität) hat. Konzentrationsabhängige Modelluntersuchungen der Ethanol- und Acetaldehydoxidation unter kontrolliertem Massentransport in Abhängigkeit vom Elektrodenpotential und der Reaktionstemperatur sind in den Kapiteln 3-4 dargestellt. Hier sollte auf die Bedeutung der Verbesserung des experimentellen Aufbaus, die das Verdunsten von Acetaldehyd minimiert und damit den Acetaldehydkonzentrationsverlust auf einem vertretbaren Maß hält, hingewiesen werden. Bei
der Ethanoloxidation nimmt der entsprechende Stromanteil der CO\textsubscript{2} Bildung mit steigender Konzentration ab, was mit Transporteffekten im “Desorptions-Re – Adsorptions - Weitereaktions-Konzept” (Details s. 1.3.2 und 3.2.2 und die darin zitierten Referenzen) erklärt werden kann. Nach diesem Konzept kann ein reaktives Produkt der unvollständigen Ethanoloxidation, z.B. Acetaldehyd (unter der Annahme, dass die Ethanoloxidation drei Hauptprodukte, nämlich Acetaldehyd, Essigsäure und CO\textsubscript{2} aufweist) erneut adsorbieren und zu CO\textsubscript{2} weiterreagieren, bevor es die Diffusionsschicht verlässt. Ähnliche Phänomene sind auch in der Heterogenen Katalyse wohl bekannt, wo eine geringere Raumgeschwindigkeit die Produktverteilung in Richtung des Gleichgewichts verschiebt. Dies stimmt mit der Zunahme des Stromanteils der CO\textsubscript{2} Bildung von 26% in 0,1 M Ethanol Lösung auf 32% in 0,01 M Ethanol Lösung (beide bei 0,6 V und 100 °C) überein. Beiträge der Re-Adsorption unvollständiger Oxidationsprodukte können bei der Oxidation von Acetaldehyd ausgeschlossen werden (Kapitel 4), da dessen einziges unvollständiges Oxidationsprodukt, Essigsäure, unter den gegenwärtigen Reaktionsbedingungen nicht weiterreagiert, was sich in der deutlich geringeren Reaktionsgeschwindigkeit der Essigsäureelektrooxidation sogar bei erhöhten Temperaturen zeigt (Kapitel 4). Neben dem Einfluss der oben erwähnten experimentellen Parameter wie Temperatur, Potential und Konzentration auf die Aktivität und die entsprechende Selektivität wird auch der pH-Wert die Aktivität der Ethanolsolektrooxidation beeinflussen. Das ist in Kapitel 5 für die Ethanolsolektrooxidation in alkalischer Lösung auf verschiedenen Elektroden dargestellt, wo der Einfluss der Temperatur und des Potentials eine wichtige Rolle für die entsprechenden Aktivitäten spielte. Der Faraday’sche Strom im stationären Zustand nimmt mit steigender Temperatur auf allen Elektroden zu, mit Ausnahme des Pt/C Katalysators bei 0,4 und 0,5 V, wo die entsprechenden Ströme im stationären Zustand zunächst mit steigender Temperatur abnehmen (unter 80 °C) und dann über 80 °C zunehmen. Die Zugabe von Ru zu Pt oder von CeO\textsubscript{2} zum Pd/C Katalysator führt dazu, dass sich das Potential, bei dem die Reaktion einsetzt, zu tieferen Werten verschiebt, was durch erhöhte Temperatur noch weiter verstärkt werden kann. Die konstanten Steigungen bei der Auftragung der logarithmischen Oxidationsraten über 1/T auf allen Elektroden deuten darauf hin, dass der geschwindigkeitsbestimmende Schritt im gesamten Temperaturbereich der gleiche ist. Die Auftragung führt zu Werten der scheinbaren Aktivierungsenergie im Bereich von 11 - 32 kJ mol\textsuperscript{-1}. Die verschiedenen Werte der
scheinbaren Aktivierungsenergie auf den jeweiligen Elektroden sind hauptsächlich auf Unterschiede in der Adsorbschicht zurückzuführen, was auch die elektrochemisch aktive Oberfläche und die massenspezifischen Aktivitäten beeinflusst. Die höchsten Aktivitäten, sowohl bezogen auf die Masse als auch auf die aktive Oberfläche, werden bei beiden Temperaturen (23 und 80 °C) auf dem Pd/C Katalysator bei einem hohen Potential von 0,7 V erhalten; für den Pt/C Katalysator werden die höchsten Aktivitäten bei 0,5 V (23 °C) und 0,7 V (80 °C) erhalten. Bei höheren Potentialen werden bessere, massenbezogene und auf die aktive Oberfläche bezogene Aktivitäten auf den monometallischen Katalysatoren erhalten (Pt/C > PtRu black und Pd/C > Pd/CeO$_2$/C).

Die in der vorliegenden Arbeit bestimmten Einflüsse der Temperatur, des Potentials, der Konzentration, des pH-Werts, die sich in Unterschieden in der Aktivität, der Selektivität (CO$_2$ Stromanteil) und den potentialabhängigen Änderungen (die Konzentration spielt auch eine Rolle) der scheinbaren Aktivierungsenergien äußern, zeigen, dass der Mechanismus der Ethanoloxidation über ein komplexes Netzwerk einzelner Reaktionen verläuft, bei dem die Gesamtaktivität (I$_F$) nur die Summe der Aktivitäten aller Teilreaktionen darstellt. Die Unterschiede in den potentialabhängigen, scheinbaren Aktivierungsenergien könnten in ähnlicher Weise von Unterschieden in den Beiträgen verschiedener Reaktionswege hervorgerufen werden.

Wenn man die systematischen Informationen über die Aktivität und Selektivität der Oxidation von Ethanol, Acetaldehyd und Essigsäure zusammenfasst, die mit den HT/HP Flusszellenmessungen in Kombination mit DEMS gewonnen wurden, kann man feststellen, dass Modelluntersuchungen unter realistischen Bedingungen wichtige und für den Betrieb praktischer Direktethanolbrennstoffzellen bedeutsame Information liefern können. Zum einen führt eine Erhöhung der Reaktionstemperatur nicht nur zu einer höheren Reaktionsgeschwindigkeit, sondern auch zu einer Abnahme der Essigsäurebildung. Das hängt damit zusammen, dass die Aktivierungsenergie für die vollständige Oxidation der Modellmoleküle zu CO$_2$ (im Vergleich zur scheinbaren Aktivierungsenergie der Gesamtreaktion) höher ist. Zudem zeigte dies auch, dass es für eine Steigerung der Leistung des Katalysators notwendig ist, die Selektivität der Oxidation von Acetaldehyd zu CO$_2$ zu erhöhen und somit die Bildung von Essigsäure, die nicht mehr weiter oxidiert werden kann und eine Sackgasse der Reaktion darstellt, zu vermeiden. Zum anderen bedeuten mögliche
Verbesserungen der Anodenkatalysatoren nicht nur, dass die Spaltung der C-C Bindung aktiviert wird, sondern auch, dass es notwendig ist, die entstehenden adsorbierten Fragmente zu CO₂ zu oxidieren. Das heißt, dass eine weitere Zunahme des C-C Bindungsbruchs nur zu einer Verbesserung der Kinetik der Gesamtreaktion führen kann (höherer Oxidationsstrom), wenn die Entfernung dieser Adsorbate nicht geschwindigkeitsbestimmend ist.

Die Messungen zur elektrochemischen Oxidation von Ethanol in alkalischer Lösung wurden in der vorliegenden Arbeit bei bis zu 100 °C durchgeführt, was über die Temperaturbeständigkeit anionischer Membranen hinausgeht. Sie erlauben es daher, kinetische Informationen über einen breiteren Temperaturbereich zu erhalten.
Appendix
Curriculum Vitae

The electronic version of curriculum vitae has been removed for reasons of data protection.
**Publications**

1. S. Sun, Z. Jusys, and R.J. Behm, Electrooxidation of ethanol on Pt-based and Pd-based catalysts in alkaline electrolyte under fuel cell relevant and transport conditions, submitted to J. Power Sources


3. S. Sun, M. Chojak Halseid, M. Heinen, Z. Jusys, and R.J. Behm, Ethanol electrooxidation on a carbon-supported Pt catalyst at elevated temperature and pressure: a high-temperature / high-pressure DEMS study, J. Power Sources, 190, 2-13, 2009
Conferences contribution

Posters

1. S. Sun, M. Chojak, Z. Jusys, R.J. Behm,
   Title: “Ethanol oxidation on carbon supported Pt catalyst at elevated temperature and pressure: an on-line electrochemical mass spectrometry study”,
   11th Ulm ElectroChemical Talks, Neu-Ulm/Germany, 2008

2. S. Sun, M. Chojak, Z. Jusys, R.J. Behm,
   Title: “Ethanol oxidation reaction at elevated temperature and pressure: on-line electrochemical mass spectrometry study”,
   42 Jahrestreffen Deutscher Katalytiker, Weimar/Germany, 2009

3. S. Sun, M. Chojak-Halseid, M. Heinen, Z. Jusys, R.J. Behm,
   Title: “Ethanol Oxidation on Carbon-Supported Pt catalyst at Elevated Temperature and Pressure: On-line Electrochemical Mass Spectrometry Study”,
   GDCh-Wissenschaftsforum Chemie, Frankfurt am Main /Germany, 2009

4. S. Sun, M. Chojak-Halseid, M. Heinen, Z. Jusys, R.J. Behm,
   Title: “Electrooxidation of small organic molecules on a Pt/C catalyst at elevated temperature and pressure”,
   Bunsen Colloquium, Reisensburg Castle, Günzburg/Germany, 2009

5. M. Chojak-Halseid, S. Sun, Z. Jusys, R.J. Behm,
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7. S. Sun, Z. Jusys, R.J. Behm,

Title: “Electrooxidation of ethanol on Pt-based and Pd-based catalysts in alkaline media at elevated temperature and pressure”,

44 Jahrestreffen Deutscher Katalytiker, Weimar/Germany, 2011

8. S. Sun, Z. Jusys, R.J. Behm,

Title: “Electrooxidation of borohydride in alkaline medium at elevated temperature and pressure”,

45 Jahrestreffen Deutscher Katalytiker, Weimar/Germany, 2012

9. S. Sun, Z. Jusys, R.J. Behm,

Title: “Electrooxidation of ethanol on Pt- and Pd-based catalysts in alkaline media at elevated temperature and pressure”,

13th Ulm ElectroChemical Talks, Neu-Ulm/Germany, 2012

10. S. Sun, Z. Jusys, A. Jäger, V. Gogel, L. Jörissen and R.J. Behm

Title: “Electrooxidation of borohydride on Pt/C catalyst in alkaline medium: model and fuel cell studies”,

13th Ulm ElectroChemical Talks, Neu-Ulm/Germany, 2012

Speech

1. Title: Electrooxidation of borohydride in alkaline medium at elevated temperature and pressure.

Katalytikertreffen - Posterworkshop "Electrochemistry in Catalysis: Experiment and Theory”,

45 Jahrestreffen Deutscher Katalytiker, Weimar/Germany, 2012

Personal skills / hobbies

Languages: Chinese (native) and English (fluent)

Sports, music, reading
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Declaration

I hereby certify that this dissertation has been composed by me and is based on my own work, unless stated otherwise. This work has not been submitted for any other degree.

Ulm, den 30. 07. 2012

(Shiguo Sun)