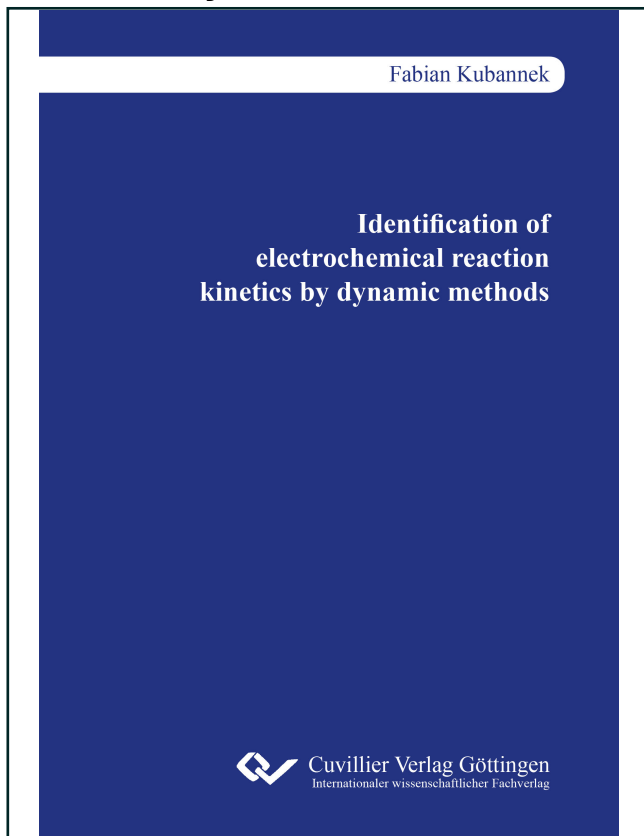




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Identification of electrochemical reaction kinetics by dynamic methods



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Chapter 1

Introduction¹

1.1 Motivation

The word 'kinetics' originates from the ancient Greek word κίνησις(kinesis) which means movement. In the fields of chemistry and chemical engineering the term kinetics refers to describing the rate of chemical reactions, i.e. the time it takes for one substance to convert chemically into another substance. Within chemical kinetics, microkinetics and macrokinetics are distinguished. Microkinetics are only concerned with the conversion rates of chemical species whereas macrokinetics additionally aim at describing the effects of heat and mass transport on these conversion rates. In this thesis, kinetics will be interpreted broadly as macrokinetics because the vast majority of electrochemical processes of practical relevance are limited by mass transfer to some degree.

The hallmark of electrochemistry is the direct link between reaction rate and electrical current that is described by Faraday's law:

$$I = rzF \tag{1.1}$$

The current I that results from an electrochemical reaction equals the product of the reaction rate r , the number of transferred electrons z , and the Faraday constant F . From this simple relation it is evident that the kinetics are key factors for the performance of any electrochemical process or device. Therefore, understanding electrochemical reaction kinetics is of general scientific interest and has high practical relevance for devices such as fuel cells, electrolysers, and

¹Parts of this chapter have been published in F. Kubanek, C. Moß, K. Huber, J. Overmann, U. Schröder, U. Krewer, Concentration Pulse Method for the Investigation of Transformation Pathways in a Glycerol-Fed Bioelectrochemical System, *Frontiers in Energy Research* 6 (2018) and in F. Kubanek, U. Krewer, Modelling and parameter identification for a biofilm in a microbial fuel cell, submitted to *Chemie Ingenieur Technik* (2018).

batteries. These technologies are often seen as key components for the transition to an economy that is powered by renewable energy sources because they allow to store large quantities of electrical energy chemically.

Knowledge-based design and systematic improvement of electrochemical processes will only become possible in future if the underlying reaction kinetics are well-understood. At the same time, a better understanding of reaction kinetics paves the way towards a deeper knowledge of electrochemical reactions and can help to elucidate fundamental questions.

A broad range of methodologies and approaches are available to elucidate electrochemical reaction kinetics. Dynamic methods are especially valuable for understanding complex electrochemical systems and for identifying their kinetics because the corresponding response signals contain significant information on the state of the electrode and allow for the decoupling of phenomena with different time constants. They have been successfully applied to various electrochemical systems. Dynamic methods with sinusoidal change in current, e. g. electrochemical impedance spectroscopy or nonlinear frequency response analysis have been used to identify the kinetics e.g. of methanol electrooxidation [1] and oxygen electroreduction [2]. Step-wise changes in current or concentration [3] have been used to study electrochemical kinetics and interaction of reaction and transport [4].

The combination of electrochemical methods and measurement of bulk concentration and surface species led to the development of various *in operando* techniques that have been shown to yield additional insights into electrode processes [5, 6]. However, usually not all state variables and quantities of interest in an electrochemical system can be accessed experimentally even with advanced analytical techniques. Modelling and simulations are suitable tools to investigate mechanisms, extract kinetic parameters and observe state variables that cannot be directly measured in electrochemical systems.

Dynamic electrochemical methods are frequently coupled with *in operando* analytical techniques and also with model-based analysis of electrochemical systems. In contrast, the combination of all three approaches is not very common. Thus this thesis is based on the hypothesis that a combination of dynamic electrochemical methods, *in operando* techniques for the detection of chemical species, and simulations, is a feasible and advantageous approach to the determination of electrochemical reaction kinetics.

1.2 Purpose and scope of this thesis

The aim of this thesis is the development of new dynamic methodologies and extension of existing methodologies to study electrochemical reaction kinetics to probe the hypothesis formulated above. In the following paragraphs, details of the chosen approach and the structure of the thesis will be laid out.

While the overall topic of this thesis is a methodological one, the developed strategies will be applied to four specific example systems which are the carbon-monoxide electrooxidation, methanol electrooxidation, acetate electrooxidation, and glycerol electrooxidation. The first two reactions are catalysed by conventional platinum ruthenium catalysts, the latter two by microorganisms in bioelectrochemical systems. For each of these electrochemical processes it will be demonstrated how the combination of dynamic current, voltage and concentration measurements yields additional insights. It will be demonstrated that concentration measurements can be used to reliably parametrise physical models of electrochemical reaction kinetics and to elucidate the effects of transport phenomena.

The reactions investigated in this thesis are discussed in ascending order of complexity of the underlying reaction mechanisms, starting from carbon-monoxide and methanol, that contain one carbon atom per molecule, via acetate, that contains two carbon atoms, ending at glycerol that contains three carbon atoms. Since the mechanism of carbon-monoxide electrooxidation is comparatively well understood whereas that of bioelectrochemical glycerol is largely unexplored, the challenges and the level of detail differ between the systems.

For all example systems, the identification of parameters from experimental data consisting of current, potential, and concentration measurements is demonstrated. In table 1.1, an overview on the methods that are used in this thesis is given. It is shown how identification procedures can account for a different number of data points or different measurement accuracies using straightforward and practical approaches as well as rigorous determination of confidence intervals and parameter interactions based on likelihood methods.

In the first part of this thesis, electrochemical oxidation reactions on porous technical electrodes are addressed where mass transfer and spatial gradients within the electrodes pose a challenge. With flux-based frequency response analysis, a novel dynamic electrochemical measurement technique is introduced. Also, for the first time, Differential Electrochemical Mass Spectroscopy (DEMS) measurements

Table 1.1: Overview on the dynamic techniques and concentration measurements employed within this thesis

System	experiment	concentration measurement	simulation
CO oxidation	potential step (CA)	DEMS	yes
methanol oxidation	CV, EIS, species flux-based FRA	DEMS	yes
acetate oxidation	CV, potential step	DEMS	no
glycerol oxidation	CV, concentration pulse (CA)	HPLC	partly

CA = Chronoamperometry, DEMS = Differential Electrochemical Mass Spectrometry, CV = Cyclic Voltammetry, EIS = Electrochemical Impedance Spectroscopy, FRA = Frequency Response Analysis, HPLC = High Performance Liquid Chromatography.

are quantitatively linked to physical modelling of electrochemical reaction kinetics and identification of rate constants.

In the second part of this thesis, the methodologies are extended to bioelectrochemical systems. One key methodological difference to the first part arises from the fact that the reaction mechanisms are less well-known and kinetic analysis does not only require to identify the values of kinetic constants for established mechanisms but also to gain a basic understanding of the system dynamics, time constants, and pathways. To this end, the first DEMS measurements on bioelectrochemical systems are performed and analysed. Additionally, it will be shown how quantitative data can be obtained and relevant conclusions can be drawn from suitable dynamic experiments even for these complex biological systems in which mechanisms are still unclear.

In **chapter 2**, the fundamentals of electrochemical reaction kinetics will be explained. First, the Butler-Volmer equation and the most common adsorption models are derived and discussed. Subsequently, a brief introduction into electrochemical energy conversion systems is given that motivates the choice of the example reactions in part one of the thesis. In the second part of the chapter, an introduction into bioelectrochemical systems is given and kinetic models for these processes are presented and compared. Finally, analytical techniques that can be used for *in operando* studies on electrochemical reaction kinetics will be briefly reviewed to explain the choice of concentration measurement methods used within this thesis.

In **chapter 3**, CO electrooxidation in a porous Pt/Ru electrode is analysed. Potential step experiments are carried out in a DEMS cell that is constructed and characterised in detail. The DEMS allows to monitor not only the transients of current density but also the CO₂ production over time. Here DEMS measurements are quantitatively correlated to simulation results from a physical model for the CO oxidation for the first time in order to identify rate constants.

In **chapter 4**, a dynamic model for the methanol electrooxidation is verified using dynamic DEMS measurements, and kinetic parameters for the model are identified. Additionally, DEMS data is evaluated in the frequency domain for the first time and the novel method of flux-based frequency response analysis is introduced. Furthermore, a detailed analysis of the contributions of different processes to the frequency response spectra and of the capabilities and limitations of the new technique is presented.

In **chapter 5**, the first DEMS measurements of an acetate oxidising biofilm anode are presented. It will be shown that Mass Spectrometric Cyclic Voltammetry and potential step experiments allow to analyse metabolic processes in the biofilm. Using this approach, internal substrate storage processes are observed and quantified.

In **chapter 6**, glycerol electrooxidation in a bioelectrochemical system is investigated. A concentration pulse methodology is applied and responses of concentration and current are analysed. This allows to separate the conversion steps between the numerous intermediates that occur in the system. It is elucidated which intermediates are important for current production, and rate constants for the metabolism of individual intermediates are determined. Furthermore, acetate oxidation in a biofilm is analysed in detail. A physical model for biofilm growth and biofilm kinetics is developed, a systematic parameter identifiability analysis is performed, and parameters as well as their correlations are determined. It is demonstrated that dynamic experimental techniques, modelling and rigorous parameter identification can also be applied to reaction systems where the exact mechanism is not clear yet.

In **chapter 7**, main findings are summarised and conclusions are drawn.

Chapter 2

Fundamentals

In this chapter, first a brief introduction into electrochemical energy conversion systems is given that motivates the choice of the example reactions in part one of the thesis. Subsequently, basic concepts of electrochemical reaction kinetics are briefly summarised. Next, the fundamentals of bioelectrochemical systems that are subject of part two of the thesis are laid out. Finally, analytical techniques that can be used for *in operando* studies on electrochemical reaction kinetics will be briefly reviewed to explain the choice of concentration measurement methods used within this thesis. Specific literature on the electrochemical reactions that are covered in this thesis, i. e. for CO oxidation, methanol oxidation, acetate oxidation in an electroactive biofilm, and glycerol oxidation in a bioelectrochemical system, is discussed in the respective chapters.

2.1 Electrochemical systems for energy conversion

Electrochemical energy systems such as fuel cells and batteries can directly convert chemical energy into electrical energy or electrical energy into chemical energy with high efficiency. Thus they have the potential to help establishing a green, CO₂ neutral economy.

The motivations for using electrochemical energy system are a high efficiency, ease of up or down scaling, potentially low emissions and the ability for flexible operation under dynamic conditions or at partial load. The reactions that are investigated in this thesis are mainly relevant for fuel cells. Thus batteries, electrolyzers, and supercapacitors will not be discussed in detail in the following.

In figure 2.1, an overview is given on common types of fuel cells and their potential applications.

Among the various types of fuel cells, hydrogen fuel cells exhibit the highest power densities and are subject to intensive research [8]. However, high volumetric

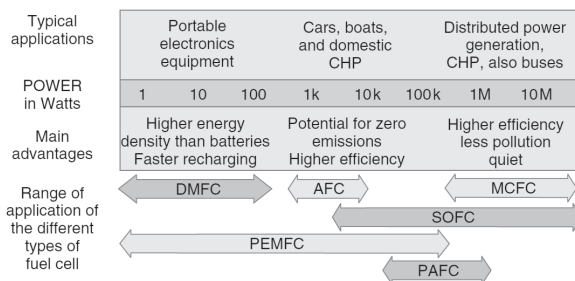


Figure 2.1: Overview on possible applications of different types of fuel cells. Reprinted from [7] with permission of John Wiley and Sons.

energy densities are not easily achieved and require storing hydrogen at conditions such as high pressure or very low temperature. This makes hydrogen storage a challenging task. Because of this, carbon containing fuels that are easier to handle are seen as promising for mobile or portable application [9]. Methanol is liquid at room temperature and can be converted in direct methanol fuel cells (DMFC) at low temperature. Larger organic molecules that contain bonds between carbon atoms can currently only be utilised at high temperatures in solid oxide fuel cells (SOFC) or molten carbon fuel cells (MCFC).

In chapter 3, the CO oxidation reaction is investigated because CO is an important intermediate in the complete oxidation of any organic molecule. Also it is known to poison the catalyst in hydrogen polymer electrolyte membrane fuel cells (PEMFC)[10, 7]. In chapter 4, the methanol oxidation reaction is investigated which is relevant for DMFC.

Bioelectrochemical systems are treated separately in the next section because many concepts and the overall state of development of the technology differ from the systems mentioned here.

2.2 Electrochemical reactions and their kinetics

In this section, basic equations that govern electrochemical reaction kinetics on solid electrodes will be explained. All these equations rely on mean-field approximations. Approaches from computational chemistry such as molecular dynamics or density functional theory are not discussed because they cannot

describe processes at non-ideal technical electrodes and at realistic time and length scales yet. For the sake of simplicity, the applicability of dilute solution theory will be assumed and concentrations will be used instead of activities. First, the Butler-Volmer equation that describes the rate of electron transfer at a solid-electrolyte interface in relation to electrode potential and reactant concentrations will be derived. Next, rate equations to describe electrochemical reactions which involve adsorbed intermediates are introduced, and the Langmuir, Temkin, and Frumkin adsorption models are explained.

2.2.1 The Butler-Volmer equation

The Butler-Volmer equation is the most common way to describe electrode kinetics. In this section the equation will be derived. The section is based on the seminal book by Bard and Faulkner [11].

The net rate r of a chemical homogeneous-phase reaction, such as reaction 2.1 from species A to species B, can be described as the difference of the rate of the forward reaction r_f and the backward reaction r_b .



The rates of forward and backward reaction are described by formal kinetics as the product of a rate constant k and the concentration c of the reactant. For reaction 2.1 this yields the following equations:

$$r_f = k_f c_A \quad (2.2)$$

$$r_b = k_b c_B \quad (2.3)$$

$$r = r_f - r_b \quad (2.4)$$

$$= k_f c_A - k_b c_B \quad (2.5)$$

According to the Arrhenius equation, the reaction rate constants can be expressed as a function of the frequency factor k_0 , the temperature T , the universal gas constant R , and the activation energy ΔG^A of the reaction:

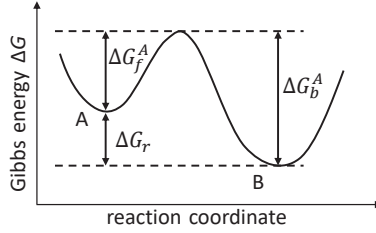


Figure 2.2: Schematic representation of Gibbs energy during a chemical reaction.

$$k = k_0 \exp\left(\frac{-\Delta G^A}{RT}\right) \quad (2.6)$$

The concept of the activation energy is shown schematically in figure 2.2. The Gibbs energy over a theoretical reaction coordinate that represents the degree of completion of the reaction from A to B must exhibit at least two local energy minima at A and B because product and educt are stable. Between the two stable species, a transition state at a higher energy level exists. The activation energy for the forward (backward) reaction ΔG_f^A (ΔG_b^A) is the difference between the Gibbs energy of the educt (product) and this transition state. Within the Transition State Theory, methods to determine ΔG^A and k_0 have been developed [11]. Since these approaches require many assumptions such as reversibility of reactions, which are often not met in real systems, and a good understanding of the transition state, the rate constant will be identified from experimental data in this thesis.

For heterogeneous electrochemical reactions at solid electrode surfaces such as reaction 2.7, the reaction rates depend on the surface concentrations of the species instead of the bulk concentrations:



$$r = r_f - r_b \quad (2.8)$$

$$= k_f c_A^0 - k_b c_B^0 \quad (2.9)$$

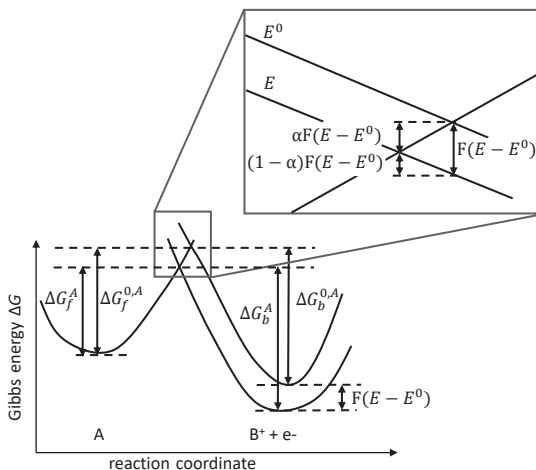


Figure 2.3: Schematic representation of Gibbs energy during a one-step, one-electron transfer electrochemical reaction at two different electrode potentials.

c_B^0 and c_A^0 denote the concentrations of A and B directly at the electrode surface. Since an electron participates in the reaction, the overall reaction Gibbs energy as well as the activation energy are functions of the potential for an electrochemical reaction. If the electrode potential is increased from the equilibrium potential E^0 to a more positive value E , the Gibbs energy of the electron on the product side is lowered. This leads to a shift in the Gibbs energy over the reaction coordinate by $F(E - E^0)$. In figure 2.3, the Gibbs energy over the reaction coordinate is compared for the two potentials. Not only the Gibbs energy of the products is reduced but also the energy of the transition state that determines the activation energies of the forward and backward reaction. The magnified section on the upper right of the figure shows how the two activation energies are affected. The activation energy of the backward reaction is increased by $(1 - \alpha)F(E - E^0)$, that of the forward reaction is decreased by $\alpha F(E - E^0)$. The factor α is called charge transfer coefficient. When the reduction reaction is defined as forward reaction, the potential change has the opposite effect, and the signs in the following equations have to be reversed. Using the Arrhenius equation, the following relation between the rate constants and the potential is established: