1 Introduction

Modern energy politics is driven by the energy turnaround reducing the amount of fossil fuels. Not only the expansion of renewable energies, but also the general reduction in energy consumption is crucial to achieve the Paris Agreement goals [1,2]. For the chemical industry, chlorine is one of the most important educts for over 60 % of all chemical products [3]. Most of the chlorine is produced in the energy intensive chlor-alkali electrolysis. In 2017 approx. 89 million metric tons of chlorine gas were produced with an energy demand of 2.5 – 3.5 MWh per ton of chlorine [4]. In total, the electrical energy demand of the chlorine production is equal to approx. 3 % of the world wide industrial electrical energy consumption [5]. In the state-of-the-art membrane process chlorine gas is produced at the anode, while hydrogen evolves at the cathode. At the first thought, this seems promising, since three valuable products, chlorine, sodium hydroxide and hydrogen, are produced in a single process. However, in reality 10 – 15 % of the evolved hydrogen is not used at all, which corresponds to the production value of a 200 MW water electrolyzer [6]. Thermal utilization or conversion back into electricity by fuel cells is not economical [7]. By the introduction of the oxygen depolarized cathode (ODC) to the system, electrical energy savings of up to 25 % were achieved [8]. Instead of evolving hydrogen, oxygen is reduced at the cathode. The byproduct, sodium hydroxide, is not affected by the usage of the new technology.

Figure 1.1 shows the comparison of the membrane (left) and ODC (right) processes schematically. In both cases the anolyte consists of saturated brine (NaCl solution) and chlorine evolves at the anode according to eq. 1.1. The positively charged sodium ions and water are able to pass the ion-selective membrane into the catholtye chamber. At the cathode the water is reduced to hydrogen and hydroxide ions according to eq. 1.2. As the negatively
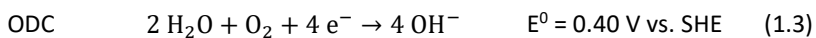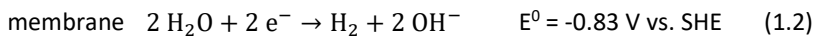
charged ions cannot pass the membrane, the product streams (chlorine, hydrogen and NaOH solution) leave the electrolyzer with high purity. Taking the standard potentials into account, at least a cell voltage of 2.19 V is required to run the electrolysis. Even after multiple iterations of improvements and minimizing all cell resistances, e.g. by zero-gap design [8], industrial cells still operate between 3 V [9] and 3.3 V [10] at 6 kA m^{-2}. Further significant reductions are only possible by changing the reaction at the cathode. By employing the ODC in the process, the evolution of hydrogen is suppressed and instead oxygen is reduced according to eq. 1.3. The amount of the produced chlorine and NaOH solution is not affected, but the required voltage decreases significantly. In theory, the cell voltage is reduced to a value of 0.96 V. Due to the low solubility of oxygen at the process conditions (80 °C, 30 − 32 wt.% NaOH) [11], the ODC needs to be designed as a gas-diffusion electrode (GDE). Within the half-cell the GDE separates an electrolyte and gas compartment as shown in Figure 1.1 on the right-hand side. In the electrolyte compartment the NaOH solution accumulates, as hydroxide ions are formed inside the ODC and sodium ions pass the membrane from the anode chamber. Oxygen is supplied in an overstoichiometric ratio reacting inside the ODC. The unreacted oxygen leaves the cell together with evaporated water from electrolyte chamber. Including all voltage loses, an industrial electrolyzer operates at 2.2 V and 4 kA m^{-2} [4].

The reactions in the process are as follows with the standard potentials (E^0) vs. the standard hydrogen electrode (SHE) according to Bratsch [12].

anode

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \qquad\qquad E^0 = 1.36\ V\ vs.\ SHE \qquad (1.1)$$

cathode

membrane $\quad 2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \qquad E^0 = \text{-}0.83\ V\ vs.\ SHE \qquad (1.2)$

ODC $\qquad\quad 2\,H_2O + O_2 + 4\,e^- \rightarrow 4\,OH^- \qquad E^0 = 0.40\ V\ vs.\ SHE \qquad (1.3)$
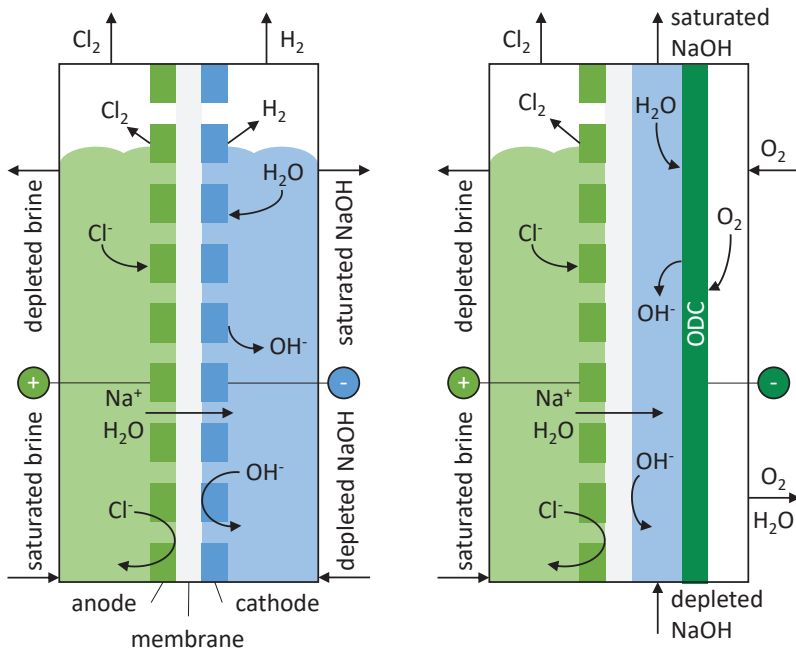
Figure 1.1: Comparison of the state-of-the-art membrane (left) and ODC (right) chlor-alkali electrolysis process. Adapted from [13].

The ODC is a complex structure with extremely high requirements, such as chemical and mechanical stability during operation, high surface area and activity of the electrocatalyst, and easy access of liquid and gaseous species without breakthrough of gas or flooding by the liquid electrolyte [14]. For the oxygen reduction reaction (ORR) silver serves as the electrocatalyst, as the activity is comparable to platinum at the given process condition [15]. The catalyst is mixed with a hydrophobic binder (most commonly polytetrafluoroethylene (PTFE)), which not only increases the mechanical stability, but also provides enough hydrophobicity to prevent the electrode from complete flooding. However, the electrolyte is still able to intrude the GDE at the more hydrophilic parts. A complex electrolyte distribution inside the GDE is created, forming the three-phase boundary and thus the available surface area for the electrochemical reaction. In Figure 1.2 a schematic overview of a single pore inside the GDE is given. Inside the pore the oxygen

and the liquid electrolyte form a contact line, resulting in a meniscus of the electrolyte on the wall. In this region the electrolyte film is thin enough for oxygen to dissolve, diffuse to the catalyst and react together with the water to hydroxide ions. This limits the electrochemical active area indicated by the gray shaded area.
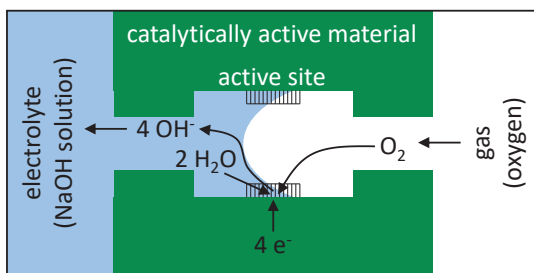

Figure 1.2: Model illustration of the three-phase boundary with transport and reaction phenomena in a single pore inside the ODC. Adapted from [13].

However, this is only a simple model conception. In reality, the structures inside the GDE a far more complex. Paulisch et al. [16] studied the pore system utilizing X-ray and synchrotron radiography, synchrotron tomography as well as focused ion beam milling and scanning electron microscopy (FIB/SEM) tomography. These techniques revealed an inhomogeneous system consisting of bigger pores connected to a complex homogeneous pore network microstructure. Examples of the FIB/SEM images are also shown in chapter 3. Neumann et al. [17] presented a pluri-Gaussian model describing the silver framework and the PTFE deposited in the pore space based on a FIB/SEM tomography. Such stochastic models allow the creation of realistic geometries in large scales, e.g. for further modeling. However, looking at Figure 1.2, it is clear, that not only the morphology of the pore system is crucial, but also the accessibility of both, liquid electrolyte and gaseous species. Therefore Kunz et al. simulated the imbibition of the electrolyte on the pore scale in 2D [18] and 3D [19]. However, their simulations require great computational resources and are only carried out on smaller scales. Coupling their simulations with electrochemical reactions would be even more challenging.

In general, for the modelling the scope of application is of fundamental importance. In their review, Kubannek et al. [20] summarized studies on

modeling the ORR in GDE through all scales. For example, Wang [21] is able to describe the morphology changes of an ODC in lithium-air batteries during discharge with a 0D model. Röhe et al. [22,23] developed a 1D model of the ODC in the chlor-alkali electrolysis focusing on the dynamic processes, while Sijabat et al. [24] described the ion transport through the membrane with a 1D model. Vasile et al. [25] focused in the distribution of oxygen near the ODC surface in proton-exchange membrane fuel cells and utilized a 3D model for that. The possibilities are endless, but a tradeoff must always be made between available computational resources, level of detail and the numbers of parameters to be determined.

This thesis focuses only on the processes inside the GDE during ORR in highly alkaline electrolyte. Already in 1965 Austin et al. [26] developed a mathematical description of electrochemical reactions in GDE based on a model system as illustrated in Figure 1.2. The gas dissolves in the electrolyte at the meniscus, diffuses to the electrocatalyst and reacts on the active side. However, only very small three-phase interfaces, and thus small limiting current densities, are achieved in this way. In order to extend the available reaction surface, e.g. Srinivasan et al. [27], Iczkowski [28] and Will [29,30] enlarged the meniscus changing it into a thin-film laying on the whole pore surface. In contrast to that, e.g. Burshtein et al. [31] and Giner et al. [32] divided the electrode in hydrophilic and hydrophobic areas. Parts of the electrode are flooded, forming the so-called flooded agglomerates consisting of electrocatalyst and electrolyte, while the other parts of the electrode transport the gaseous species to the reaction sides. In 1975 Cutlip [33] combined both model approaches developing the so-called thin-film flooded agglomerate (TFFA) model. The electrode consist of hydrophobic gas channels and flooded agglomerates covered with a thin-film of electrolyte. The gaseous species diffuses through the gas channels, dissolves at the thin-film interface and diffuses to the flooded agglomerate, where the reaction takes place. Wang and Koda [34,35] adapted the model to the ORR for the chlor-alkali electrolysis. The electrolyte intrude the GDE in a finger shaped way, forming the flooded agglomerates. In between these electrolyte fingers the gaseous oxygen is able to diffuse to the reaction side. Later, Pinnow et al. [36] extended

the model mainly by considering binary Maxwell-Stefan diffusion in the gas and electrolyte phase and validated it with half-cell polarization curves. However, recent studies by Botz et al. [37] showed, that the electrolyte transport in the GDE was underestimated. Further, the electrolyte distribution was unknown, due to the lack of operando experiments at this time. Thus, the geometric parameter were adjusted to match the half-cell experiments. In this thesis, the model of Pinnow et al. [36] is extended progressively to eliminate the unknown parameters. In the end, the improved model describes the processes inside the GDE even better and will give further insights.

The present thesis is structured into published manuscripts, which each contribute to the overall topic as follows:

- **Chapter 3** describes the influence of the PTFE content on the GDE. The techniques to analyze the pore system and the electrochemical performance via half-cell experiments are introduced. A commercially available half-cell and an in-house test set-up, designed for stationary conditions at the GDE, are utilized. The latter allows the application of pressure gradients between electrolyte and gas compartment. The experiments show that the electrolyte distribution is of fundamental importance, but cannot give any information of the shape and intrusion depth of the electrolyte.

- **Chapter 4** describes the development of the improved TFFA-model. The electrolyte distribution is determined independently from half-cell polarization curves during synchrotron operando experiments. Further, the electrolyte transport is considered adequately and all relevant physical parameters are integrated as correlation equations in dependence of the actual electrolyte concentration inside the GDE. As a result, the polarization curves can be predicted over a wide range of oxygen and electrolyte concentrations, while reducing the amount of unknown fitting parameter.

- **Chapter 5** addresses the question of whether the intrusion depth of the electrolyte can be determined. Graded electrodes, consisting of nickel diffusion layers and silver reaction layers, were manufactured according to the assumed subdivision of the TFFA-model. In this way, the effective

intrusion depth of the electrolyte is determined experimentally and compared with the simulation results. This gives further insights on the actual electrolyte distribution.

2 Overview of the publications

The following publications were submitted and published in "peer-reviewed" scientific journals and are an integral part of this doctoral thesis.

1. D. Franzen, B. Ellendorff, M. C. Paulisch, A. Hilger, M. Osenberg, I. Manke, T. Turek; Influence of binder content in silver-based gas diffusion electrodes on pore system and electrochemical performance, J. Appl. Electrochem., 49, 705–713 (2019).

   The actual impact factor of the Journal of Applied Electrochemistry is 2.398 (2019). The contribution of the first author was to design and conduct the electrochemical experiments and to prepare the manuscript. B. Ellendorff manufactured and physically characterized the Electrodes. M. C. Paulisch, A. Hilger and M. Osenberg executed FIB/SEM-tomography and reconstruction supervised by I. Manke. T. Turek advised in the experiment conception and contributed to writing the manuscript. This publication is reprinted in chapter 3 and describes the influence of the binder content on the pore system and the electrochemical performance. The utilization of the pore system and thus possible electrolyte distributions are discussed. Additionally, the experimental setup as well as physical characterization techniques are described in detail.

2. D. Franzen, M. C. Paulisch, B. Ellendorff, I. Manke, T. Turek; Spatially resolved model of oxygen reduction reaction in silver-based porous gas-diffusion electrodes based on operando measurements, Electrochim. Acta, 375 (2021) 137976.

   The actual impact factor of the Journal Electrochimica Acta is 6.216 (2020). The contribution of the first author was to design and conduct the electrochemical experiments, develop the mathematical model and

to prepare the manuscript. M. C. Paulisch conducted and evaluated the operando experiments as well as supported to prepare parts of the manuscript concerning the operando experiments supervised by I. Manke. B. Ellendorff manufactured the Electrodes. T. Turek advised in the experiment and model conception and contributed to writing the manuscript. This publication is reprinted in chapter 4 and describes the development of the improved TFFA-model. The shape of the electrolyte distribution is implemented on the basis of the first available operando synchrotron experiments. Further, the electrolyte properties are spatially resolved, allowing a description of all processes for different NaOH and oxygen concentrations.

3. D. Franzen, C. Krause, T. Turek; Experimental and model-based analysis of electrolyte intrusion depth in silver-based gas diffusion electrodes, ChemElectroChem, 8, 2186–2192 (2021).

    The actual impact factor of the Journal ChemElectroChem is 4.154 (2019). The contribution of the first author was to design and evaluate the experiments, as well as to adapt the mathematical model. C. Krause prepared the electrodes and conducted the experiments. T. Turek advised in the experiment and model conception, and contributed to writing the manuscript. This publication is reprinted in chapter 5 and describes the influence of the electrolyte intrusion depth on the electrochemical performance. The reaction zone is precisely defined by specially designed graded electrodes. The geometrical parameters of the graded GDE can be transferred to the previously provided TFFA-model, resulting in a model-supported analysis of the effective penetration depth of the electrolyte.