# Chapter 1

# Introduction

The increasing energy demand of the world presents a challenge to develop renewable, carbon-neutral and cost-competitive alternatives to fossil fuels [1]. These energy sources will be required in the scale of terawatts to minimize the environmental impact of the global energy use. The main new and clean energy sources worldwide are currently wind and solar power. Approximately $539\,GW$ of wind power and $402\,GW$ of solar power was the total installed capacity worldwide by the end of 2017 [2]. The addition of these renewable sources into an existing electric grid gives rise to new challenges, such as storing and utilizing the surplus energy as well as long-term energy supply reliability. Therefore, a storage system which is neither limited in capacity nor has a maximum storage duration is required.

Hydrogen ($H_2$) is gaining relevance as a twenty-first century energy carrier. Its energetic potential lies in the ability to not only serve as an energy source, but also to act as an energy storage, transport or conversion medium. Even though $H_2$ is the most abundant element in the universe, it cannot be found in its pure state on our planet. About $95\,\%$ of the produced hydrogen worldwide ($97.44\,MMT$ [3]) is based on fossil fuels, mainly natural gas [4]. In order to keep the $H_2$ generation carbon neutral, hydrogen has to be obtained from renewable sources such as thermochemical biomass processes or water electrolysis powered by electricity from renewable sources. There are different types of water electrolysis systems with their specific benefits which will be highlighted in the following chapter. However, most of these processes are still limited to some research and development projects. From a technological point of view, only the alkaline electrolysis (AEL) and the polymer electrolyte membrane electrolysis (PEMEL) are at present sufficiently developed for large-scale production rates of renewable $H_2$ [5]. Until recently these electrolysis systems have mostly been applied for continuous industrial processes like the production of high quality chemicals or as a basis for synthetic vehicle fuels. However, both these application areas did not require the electrolysis process to be flexible in terms of dynamic operation. The ability to quickly ramp up or down the hydrogen generation becomes an important factor for the successful grid integration of such systems. Thus, even though electrolyzers have be known for decades and widely applied, there is a demand for innovation. The systems have to adapt to be able to adequately respond to power production fluctuations [6].

Besides the ability to serve as a grid stabilization tool, renewable $H_2$ from electrolysis has the potential to serve as the basis for further conversion processes. The term "Power-to-X" describes the conversion chains from electricity over $H_2$ to value-added materials such as synthetic gases or fuels. The flexibility of $H_2$ as a component enables a cross-sectoral reform of the society towards a carbon neutral future. Especially, the process of carbon dioxide ($CO_2$) reduction and further methanation is of great interest. On the one hand, this conversion can use captured, excess $CO_2$ from industrial exhaust gases or directly from the atmosphere [7]. On the other hand, the conversion from hydrogen to methane enables the use of the national gas grid. It can simultaneously act as an already existing storage as well as transport system which leads to significant cost benefits. Additionally, the gas grid could relieve the partly overloaded electrical grid.

This thesis investigates the influence of various, rectified current profiles on an alkaline electrolysis. A process current source (PCS), provided and developed by *Steffen Bintz* from the *Institute for Power Electronics and Electrical Drives*, functions as a programmable rectifier. With the help of this power source, it is possible to provide the electrolysis with modified current output forms in order to reduce overpotentials in the electrolysis process. The aim is to decrease the energy consumption compared to conventional rectifier models and their characteristic current profiles and thus to reduce the operation costs. An energetic performance increase of the alkaline electrolyzer is reached by a higher factor of rectification from the transistor-based PCS compared to conventional thyristor-based systems. Furthermore, it is presented how short current pulses can tackle the increasing bubble resistance at high current densities. Therefore, enabling the AEL to operate above the conventional maximum load which could improve the grid stability in times of too much energy generation. However, not only high load scenarios are problematic. While provided with low load current profiles from conventional rectifiers, the electrolyzer showed an increased energy consumption as well as oxygen impurities in the hydrogen gas. Experiments highlighted that this results from higher ripples in the output current provided by the rectifier system. Such a behavior would strongly limit the dynamic operation possibilities of AEL, if connected to the national grid.

The generated $H_2$ from the partly optimized electrolysis system can be stored or converted into synthetic methane. An experimental setup, mainly consisting of a low-pressure and low-temperature glow discharge plasma reactor, is used to reduce $CO_2$ in order to form methane. An ancillary ceramic ion conductor is employed to extract oxygen ions from the plasma, reducing the amount of recombination with the carbon monoxide ($CO$). Afterwards, the methane could be transformed into various biofuels for combustion engines.

By combining both of these systems, it is shown how a power-to-gas (PTG) conversion chain can be operated, only by the use of electricity and without additional catalytic platinum group metals or other scarcely available components. The developed system can be scaled up and then be integrated to the electrical grid with the benefit of cost-reduced grid services as well as electrochemical long-term storage potential.

The goal of this thesis is fabrication and study of modified direct current profiles for alkaline water electrolysis and the effects on the electrochemical system behavior. Specifically modulated current pulses are employed to enhance or hinder chemical processes inside the electrolysis cell. The characterization of the electrochemical double layer and the gas bubble evolution at the electrodes are required to successfully design current forms with a beneficial impact. For these steps, an electrochemical impedance spectroscopy provides information on the system, while a newly designed process current source enables adjustable current output forms at will. Furthermore, this device can provide an almost perfect direct current at all loads stages and thus functions as a reference for rectifier performance. Conventional rectifier structures are analyzed and their output currents are simulated over a wide range of operation. The replicated current forms are subsequently scaled and applied to a self-designed laboratory scale alkaline electrolyzer. These profiles enable the investigation of specific current forms on performance reducing overpotentials inside the cell. A comparison of the energy consumption and hydrogen gas quality for different load stages can provide information on required specifications of rectifier systems for future integration in dynamical electric grids.

Hydrogen storage faces different challenges resulting from the small molecule size as well as the low volumetric energy density. However, the conversion to synthetic methane can circumnavigate these factors for large-scale energy storage areas. A plasma-based methanation process with a ceramic ion conductor for oxygen ion extraction is to be developed and characterized. Firstly, the reduction of carbon dioxide has to be achieved so that a subsequent hydration can take place. The aim is to obtain a proof of concept for the methanation approach.

# Chapter 2

# Theoretical Principles

This chapter gives a theoretical background as the basis for the experiments and investigations presented in the following chapters. The first section describes conventional rectifier technologies as used for commercial electrolysis projects with a focus on six-pulse and twelve-pulse bridge rectifiers as well as a two-staged AC power controller with a passive six-pulse bridge. The following section summarizes the general properties of water electrolysis covering topics such as hydrogen and oxygen evolution reactions as well as thermodynamics and electrode kinetics of the electrolysis process. An additional focus lies on the gas bubble evolution, the electrochemical behavior at the electrode as well as gas bubble nucleation. Furthermore, the bubble growth and dissolution processes are presented in detail. This subsection concludes with an explanation of the main electrolysis technologies as well as the advantages and challenges for future applications. In the last section, plasma processes for $CO_2$ reduction and subsequent methanation are introduced providing an overview of the various plasma technologies as well as industrial carbon dioxide sources.

## 2.1 Rectifier

Rectifiers are electrical devices that convert alternating current, which periodically reverses direction, to direct current which flows in only one direction. Due to the alternating nature of the input sine wave signal, the process of rectification alone generates a direct current that, though unidirectional, consists of pulses. Rectification may serve in roles other than to produce direct current for use as a source of power. For example, detectors of radio signals serve as rectifiers as well. In gas heating systems flame rectification is used to detect the presence of a flame. However, this section deals with conventional rectifier systems as employed for various power supply applications.

### 2.1.1 Rectifier Topologies

Applications areas like electrolysis, direct current (DC) furnaces and plasma torches require high-current power supplies at lower voltage levels. Regarding the output DC voltage, rectifiers can be separated into two main categories. Namely, variable- and fixed-output-voltage type systems [8–10]. Rectifiers with a fixed DC bus voltage are mainly used in the AC-AC conversion process for motor drives, uninterruptible power supplies and a lot of more applications. The flexibility of these systems and the various applications have driven the research on these rectifier systems steadily. Thus, they stand at an advanced stage with a good power factor, low current total harmonic distortion (THD), low DC-voltage as well as high power density [8]. On the contrary, variable DC-voltage rectifiers as a niche category are still dominated by multi-pulse rectifiers using thyristor or even diode technologies [8, 9, 11–13]. There are various requirements for rectifier systems, ranging from output voltage over current ripple and power factor to criteria as reliability and efficiency. Diode- and thyristor-based rectifiers are commonly operated in high-current applications (up to $25\,kA$) because of their proven reliability, robustness, long life, simplicity and availability of suitable rating of semi-conductor switches. In the industry, they use different configurations depending on the power levels as well as on the application-specific requirements [11–13]. The following subsections will focus on conventional rectifiers as used in current day electrolysis systems.

#### 2.1.1.1 Six-pulse Bridge Rectifier

The six-pulse bridge rectifier (B6C) structure is a combination of two three-pulse center tapped circuits connected in serial. Their main task is the transformation from provided three-phase voltage into direct voltage. The six-pulse bridge rectifier is a line-commutated converter, thus the commutation from one active leg to the other is driven by the electrical grid. There are two versions of this basic rectifier topology, a controlled one that uses thyristors and an uncontrolled variant with diodes as switches. The thyristors are able to increase or decrease the output voltage by choosing the time of activation, also called firing angle. Figure 2.1 shows the secondary side equivalent circuit of a B6C rectifier.

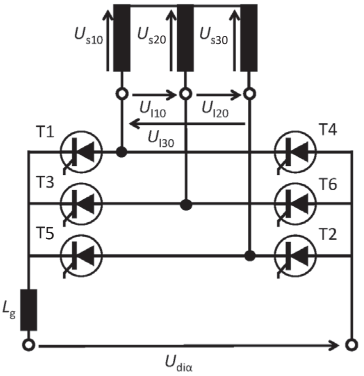

**Figure 2.1:** Schematic of a six-pulse, controlled bridge rectifier with commutating inductance (B6C).

The thyristors are divided into two groups. Thyristors T2, T4 and T6 belong to the anode connection point whereas the valves T1, T3 and T5 belong to the cathode connection point. If the thyristors are fired at the first possible point of time, it is called natural ignition. By varying the firing angle, it is possible to establish a voltage control.

#### 2.1.1.2 Twelve-pulse Bridge Rectifier

Figure 2.2 displays a twelve-pulse bridge rectifier (B12) consisting of two six-pulse parallel bridges.

A three-winding transformer with a star- and delta-connection at the side of the power controller is used for this topology, marked with the indices $Y$ and $\Delta$. These different types of connection result in a phase difference of $\frac{\pi}{6}$ between the corresponding line-to-line voltages of the two six-pulse units. The interphase transformer is required for the reliable firing of the thyristors. This structure still has a simple layout with low power losses and low cost components, although the parallel use of thyristors can lead to complications and results in high reactive power load for the feeding electric grid. The controllability lies between 20 % and 100 % of the nominal power and has an efficiency of 98 % at normal operating conditions.

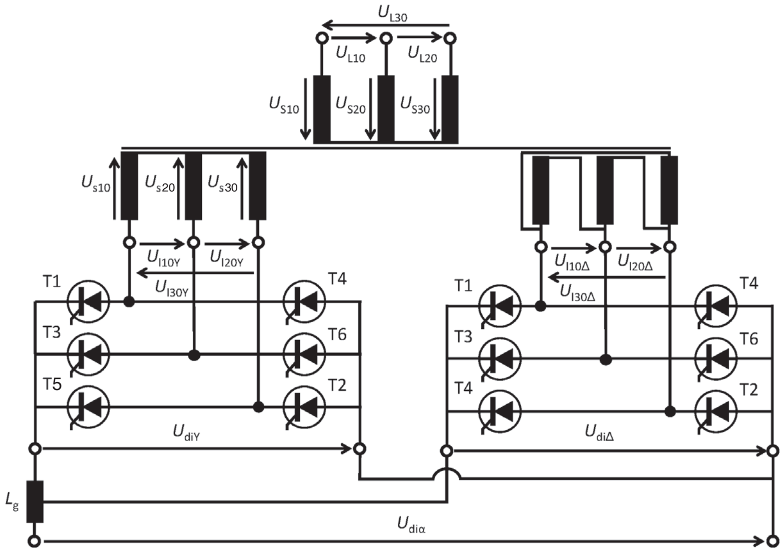

**Figure 2.2:** Schematic of twelve-pulse, controlled bridge rectifier with commutating inductance (B12).

### 2.1.1.3 Two-staged AC Power Controller with Passive Six-pulse Bridge

Another commonly used rectifier topology consists of a six-pulse, non-controlled bridge unit in series with a controlled thyristor based six-pulse bridge (W3M) as shown in Figure 2.3.

This structure differs from the previous two, because it is controlled by the transformer sided, two-staged power controller. Simultaneously, the six-pulsed diode bridge rectifies the voltage at the secondary side. On the one hand, this structure enables a controllability over the entire load range as well as over a low reactive power feedback to the electric grid and only needs control for the thyristor unit.

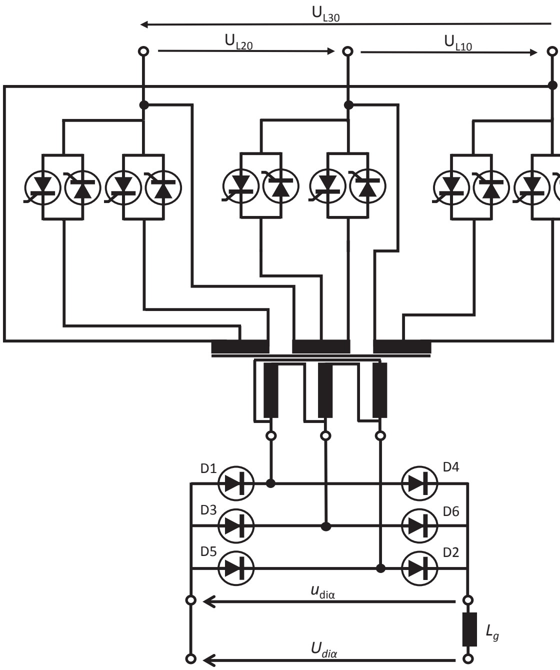

**Figure 2.3:** Schematic of a non-controlled, six-pulse bridge in serial with a controlled, thyristor based six-pulse bridge (W3M).

On the other hand, it has increased losses due to the serially connected units and a higher value for the current link. The efficiency of the rectifier depends on its point of operation and varies between 95 % and 98 %.

## 2.2 Water Electrolysis

The basic principle of water electrolysis is the circulation of a direct current through water in order to split its molecules into $H_2$ and $O_2$. This current flows between two electrodes, separated and immersed in an electrolyte which increases the ionic conductivity. The key features of electrodes for water decomposition are a high conductivity, corrosion resistance, catalytic properties as well as a suitable structure.

It is important that the electrolyte shows no side reactions during the electrolysis process, such as reactions with the electrodes itself. Both electrodes are electrically isolated from each other by a separator, often a semi-permeable membrane. Furthermore, the separator prevents the recombination of the generated $H_2$ and the $O_2$. Nevertheless, the used diaphragm should have high ionic conductivity as well as a high chemical and physical resistance. All mentioned components are the elements that configure a basic electrolytic cell. The half-cell reactions occurring at the cathode

$$2H^+ + 2e^- \longrightarrow H_2 \tag{2.1}$$

and respectively at the anode

$$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-, \tag{2.2}$$

lead to the resulting global reaction

$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2. \tag{2.3}$$

In order to keep this electrochemical reaction process going, a number of barriers have to be overcome. These so called overpotentials require a sufficient amount of supplied energy as extra input. The negative effects include activation energies of the electrochemical reactions occurring on the electrodes surfaces, electrical resistance of the circuit, the resistances attributed to the ionic diffusion inside the electrolyte and the membrane as well the availability of active electrode surface due to partial blocking by growing gas bubbles. The thermodynamics, kinetics and the transport principles of the overpotentials have to be analyzed in order to be able to reduce specific loss mechanisms. The simplest way to show these overpotentials is in an electrical circuit analogy of resistances as presented in Figure 2.4.

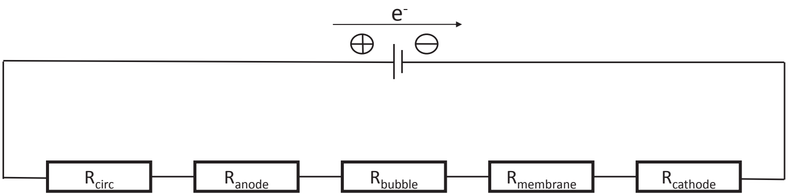

**Figure 2.4:** Serial connected ohmic resistances, representing the loss mechanisms in an alkaline electrolysis system.