Temperature and pressure effects on the electrochemical CO2 reduction

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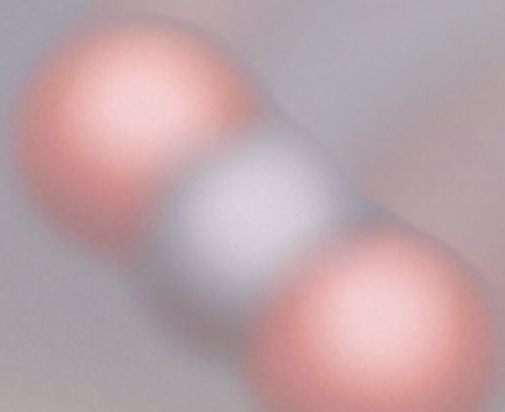
Introduction



1.1 General context

One of the largest and most pressing issues of this time is the changing climate due to manmade emissions of greenhouse gasses, most importantly CO_2. Since the industrial revolution in 18th century, atmospheric CO_2 concentrations have risen with 50 percent to over 420 ppm currently[1]. In fact, more than 40 percent of the historic CO_2 emissions has been emitted since the turn of the last century[2]. Increasing atmospheric CO_2 concentrations leads to global warming, increased extreme weather events such as storms, droughts and floods, ocean acidification, melting of glaciers and pole ice and sea level rise[3]. This decreases the livability of earth for many humans around the world and harms nature and its ecosystems severely[3].

To limit the effects of climate change, the world should stay below 1.5 °C global warming compared to the pre-industrial era, as agreed upon in the Paris agreement. To reach this ambitious goal, or at least limit global warming as much as possible, a rigorous change is needed in the way modern society uses energy and materials. A transition is needed from a world based on fossil fuels to a world based on renewable resources. For the energy transition, a shift takes place from gas and coal based energy supply to an energy system build on solar and wind energy. Mobility is shifting from petroleum-based to electric cars and buses. However, for some forms of transportation, such as aviation and freight ships, liquid based fuels might still be necessary, due to the advantages of their high energy density [4–7].

Fossil resources are not only used to produce energy, but also as feedstock for many materials society uses, as the entire chemical industry[8] and also the steel industry are based on them. Therefore, not only an energy transition is needed, but also a material or chemical feedstock transition is necessary. Due to the scale of this transition, many solutions are needed simultaneously, especially as climate change is only one of the parameters to stay within the planetary boundaries[9]. Besides improving plastic recycling and the use of biomass as feedstock, using CO_2 as feedstock [10,11] can give a vital contribution to make both the energy and material transition possible. More research is necessary [9] to improve technologies that use CO_2 as a feedstock to make these transitions possible and to turn CO_2 from a pollutant into a valuable resource.

1.2 Electrocatalysis

With the acceptance that climate change is one of the major issues of this time and that an energy transition is needed to stop climate change, electrocatalysis has gained more attention recently. While in thermocatalysis reactions are driven by temperature and pressure, in electrocatalysis the energy to drive a chemical reaction is provided by electricity. This is interesting as the new renewable energy sources as wind and solar energy produce primarily electrical energy in contrast to the old fossil fuel energy sources which typically produce heat. Electrocatalysis is part of the broader field of electrochemistry, which is defined as the study of the transformation of electrical energy in chemical bonds and vice versa [12]. Electrochemistry is an old field as the first experiments generating hydrogen from electricity where conducted at the end of the 18th century, shortly afterward followed by the production of the first battery [13]. Besides electrocatalysis and batteries, the field also includes sensors such as glucose sensors, corrosion processes and electroplating techniques, for example to produce cans [12].

Catalysts are materials that enable or enhance a chemical reaction, by lowering the reaction barrier. Electrocatalysts use electricity to convert molecules as H_2O, CO_2 and N_2 into energy carriers or chemical building blocks such as hydrogen, CO, ethylene and ammonia. In general, electrocatalysts can be divided into homogeneous and heterogeneous catalysts. Homogeneous catalysts facilitate a redox reaction in the liquid phase[14]. This thesis only discusses heterogeneous catalysts, for which the electrochemical reaction takes place at the surface of the electrode, which is often a metal[14].

The electrochemical conversion is performed in a device known as an electrolyser. On the cathode material a reduction reaction takes place in which the electrode provides electrons to the reactants. On the anode material an oxidation reaction takes place in which electrons are transferred from the reactants to the electrode material. The oxidation and reduction reaction are performed simultaneously to complete the electrical circuit. For example, in a water electrolyser, H_2O is split into hydrogen on the cathode and oxygen on the anode according to the following half reactions:

$$2\,H_2O + \ 2e^- \rightarrow \ H_2 + 2\,OH^- \qquad (1.1)$$

$$2\,H_2O \rightarrow \ O_2 + 4\,H^+ + 4\,e^- \qquad (1.2)$$

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad (1.3)$$

The two half reactions in equation 1.1. and 1.2 are required to complete the total reaction given by equation 1.3. In an industrial electrolyser, the cathode and anode are the only two electrodes. However, our experiments in the lab are performed with a three electrode system to gain more fundamental understanding by studying one specific half reaction. In this configuration, the working electrode is the electrode that carries out the reaction of interest. The counter electrode completes the circuit and the reference electrode is used to determine the potential applied to the working electrode[15], as illustrated in Figure 1.1. In this thesis, the cathode is always the working electrode, making the anode the counter electrode. We will discuss the reference electrode in more detail below. All electrodes are placed in the electrolyte. This is an electrically conducting medium and for electrocatalysis often consists of water with certain concentrations of salt. Throughout this thesis, common electrolytes are 0.1 M sodium bicarbonate or potassium bicarbonate. During electrolysis, the cathode and anode are often separated with a membrane, which prevents products to cross over to the other electrode and react there. The electrolyte at the cathode side is called the catholyte and the electrolyte on the anode side the anolyte.

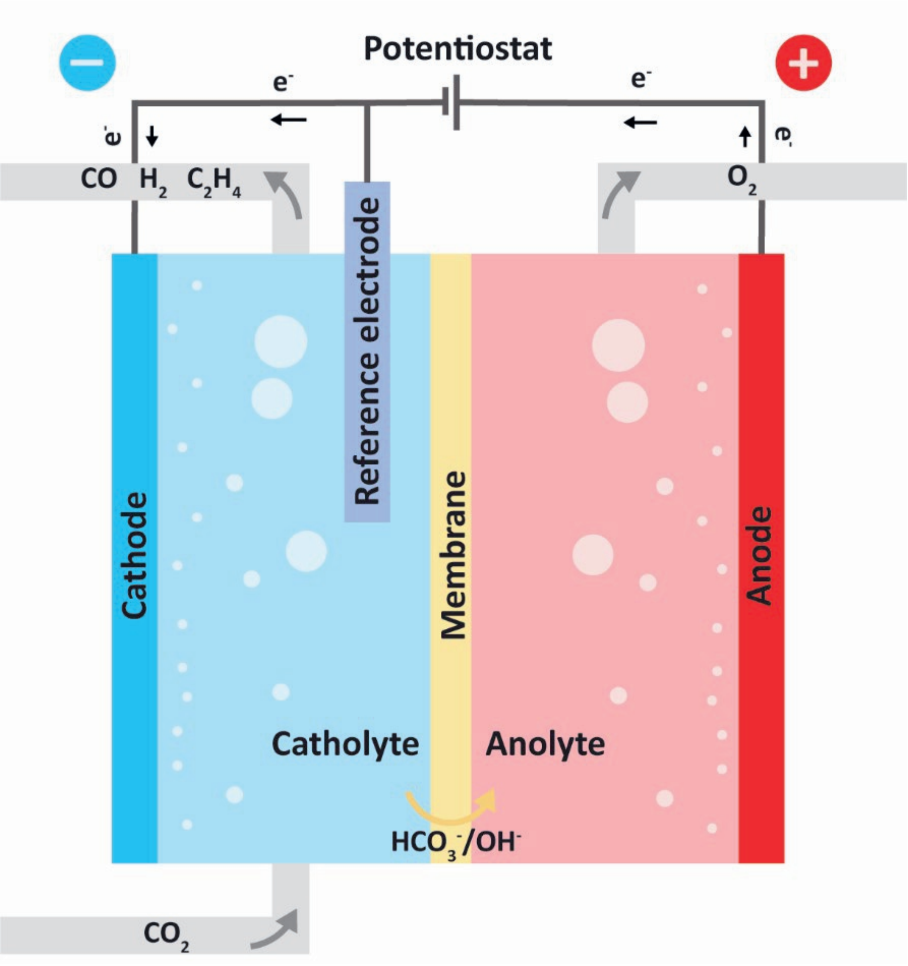


Figure 1.1 Pictorial representation of a three-electrode H-cell configuration for electrochemical CO_2 reduction where the cathode and anode are separated by an anion-exchange membrane

The potential at which a half reaction such as equation 1.1 is at thermodynamic equilibrium, is given by the Nernst equation:

$$E = E^0 - \frac{RT}{nF}\ln(Q) \qquad (1.4)$$

in which E is the potential, E^0 the standard equilibrium potential, R the gas constant, T the temperature, n the number of electrons transferred, F Faraday constant and Q the reaction quotient, which is derived from the activities of all electroactive species. Since the Nernst potential describes equilibrium, an additional potential needs to be applied to overcome several barriers and resistances, which is called the overpotential. Some of these barriers are due to the reaction and a good catalyst minimizes the overpotential needed to drive the reaction. Other resistances can come from the electrolyser design, such as the ohmic drop due to the resistance of the electrolyte. These losses can be minimized by design of the electrolyser and electrolyte, and by optimizing process parameters such as temperature. Fundamental electrocatalysis research focuses on understanding and optimizing the catalyst and its environment to minimize the overpotential needed, while electrochemical engineering focuses more on optimizing the process parameters and cell design.

1.3 Electrochemical CO_2 reduction

Since the seminal reports of the electrochemical CO_2 reduction reaction (CO2RR) by Hori et al. in the 80s of the last century [16–18], the interest for this reaction accelerated around the beginning of this century due to the urgency of climate change. Heterogeneous CO2RR catalysts are generally classified in four groups [19,20]. Au, Ag and Zn produce mainly CO from CO_2, while Pb, Sn, In, Cd, Hg and Tl produce mainly HCOOH via reaction 1.5 and 1.6, respectively. CO can be used in syngas as an important chemical precursor for numerous reactions such as to produce hydrocarbons via the Fischer-Tropsch reaction[21] or to produce methanol in the methanol synthesis process[22]. HCOOH can be used as fuel[23] or hydrogen carrier[24] although it is nowadays mostly used as intermediate or additive in industrial applications[25]. Cu is a unique catalyst for electrochemical CO_2 reduction as it can go beyond these simple C1 products and make C2+ products in which a C-C bond is generated. Products can be ethylene and ethanol, as given in equations 1.7 and 1.8, but Cu can form a scala of other products such as methanol, 1-propanol and acetate [26]. Some of these products are of particular interest within the material and energy transition as they can be used as fuel (methanol/ethanol) or as feedstock for the chemical industry (ethylene). The last group of CO2RR catalysts, such as Pt, Fe and Ni, is not very active in CO_2 reduction but rather produces H_2 via the competing hydrogen evolution reaction (HER) in equation 1.1. HER is active in a comparable potential region to CO2RR, so for active and selective CO2RR catalysts, HER always needs to be minimized.

$$CO_2 + H_2O + 2\,e^- \rightarrow CO + 2\,OH^- \qquad (1.5)$$

$$CO_2 + 2\,H_2O + 2\,e^- \rightarrow HCOOH + 2\,OH^- \qquad (1.6)$$

$$2\,CO_2 + 8\,H_2O + 12\,e^- \rightarrow C_2H_4 + 12\,OH^- \qquad (1.7)$$

$$2CO_2 + 9\,H_2O + 12\,e^- \rightarrow C_2H_5OH + 12\,OH^- \qquad (1.8)$$

A good CO2RR catalysts needs to be active, meaning the current density that goes towards CO2RR products such as CO and HCOOH is high and the overpotential is minimized. Moreover, the catalyst needs to be selective. This means that the competing HER should be minimized, which is difficult on many catalyst materials. As Cu can produce many different products, selectivity in this case also means that the Cu catalyst produces primarily one of the possible CO2RR products, which has shown especially challenging due to the complex reaction network. Lastly, for commercialization, a good catalyst should be stable and be able to operate for thousands of hours [27–30]. Many parameters have been studied in recent years to improve the CO2RR catalysts on all these aspects. Some parameters are related to the catalysts itself, such as the facet dependence [31–34], morphology [35–39], alloying [40–44] and surface modifications [45–50], while others are related to the environment of the catalyst, primarily the electrolyte, such as cations [51–54], anions [55–58], pH [59–63] and electrolyte concentration [64–66]. These studies are often performed on small scales, but when moving towards industrialization, other parameters become important as well, such as cell configuration, temperature and pressure.

Electrochemical CO_2 reduction is typically performed in neutral aqueous media. Acidic electrolytes are avoided as they enhance hydrogen evolution, although recently more studies have been performed at low pH with promising results [67–70]. Alkaline electrolytes are avoided in studies using a H-type cell as the OH^- would react with the CO_2 forming bicarbonate. With the use of gas diffusion electrodes, the CO_2 gas is not bubbled through the electrolyte, and alkaline electrolytes are commonly used [71–74]. In this thesis, all experiments are performed using a H-type cell and thus neutral bicarbonate electrolytes are used. Moreover, as we are interested in the performance of the catalyst and not the entire electrolyser, a three electrode system is used in combination with IR correction to overcome the Ohmic losses of the electrolyte. Furthermore, simple metal foils and wires are typically used as working electrodes to limit the complexity of the system studied. Electrochemistry in general and CO2RR specifically are typically performed at ambient conditions, as this is often seen as one of the advantages of electrocatalysis over thermocatalysis. However, for industrialization [75–77], this might not be the most suitable condition as electrolytes are expected to heat up due to thermal losses [78–80] and warm feedstocks, and higher temperatures can lower the overall cell potential [76,77]. Therefore, it is important to fundamentally investigate the effect of temperature and pressure on the electrochemical CO_2 reaction.

1.4 Temperature as parameter in electrochemistry

Thermoelectrochemistry is "the branch of electrochemistry which is devoted to the influence of temperature as an independent variable on the charge transfer reaction at condensed interfaces" as defined by Gründler et al.[81]. Within electrocatalysis, there are some studies on the effect of temperature and pressure on several reactions, such as the hydrogen evolution reaction [76,82–84], oxygen evolution reaction [85–88], oxygen reduction reaction [89–91] and CO_2 reduction reaction [17,92–95]. However, temperature and also pressure are still very understudied parameters in electrocatalysis and systematic studies are scarce.

When pressure and especially temperature are changed in electrochemical systems, several factors have to be considered. As seen in equation 1.4, the potential of a reaction is dependent on the temperature, especially as besides the explicit T in the Nernst equation also the standard potential and activities are dependent on temperature. This is important to consider when measuring a potential as also the reference electrode potential depends on temperature [81,96]. In thermo-electrochemistry, an external reference electrode can be used , where the reference electrode operates at room temperature and is connected to the electrolyser with an electrolyte bridge [96]. However, due to the difference in temperature, the external references experience a thermal liquid junction potential [81], for which an empirical correction has to be made to determine the potential precisely [96,97]. Therefore, we use internal reference electrodes in this thesis. Internal reference electrodes are used at the same temperature and pressure as the rest of the electrochemical system and the effect of temperature can be calculated with the Nernst equation (1.4). As SHE is defined 0 at all temperatures,[81,97] the RHE is the most easy internal reference electrode to use. At ambient pressures we therefore us this reference electrode in this thesis. However, at elevated pressures, a Ag/AgCl reference had to be used and more corrections have to be made to compare results on an SHE scale.

Temperature and pressure influence many other parameters of the electrochemical system. During CO_2 reduction, an important one is the CO_2 solubility, which decreases with increasing temperature. This can significantly influence the catalytic reaction as many CO2RR catalysts are sensitive to the bulk concentration of CO_2. As the CO_2 pressure also influences its solubility, it is possible to gain more insights with partial pressure experiments, by deconvoluting the direct effect of temperature with the indirect effect via the CO_2 solubility. Other parameters that are influenced by the temperature are the pH, diffusion coefficients and viscosity [81] which can influence the reaction itself, the reference potential and the mass transport during the reaction. Most importantly for catalysis, temperature influences the kinetics of the reaction via the Arrhenius equation, where k is the rate constant, A the pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature:

$$k = A\, e^{-\frac{E_a}{RT}} \qquad (1.9)$$

1.5 Outline of this thesis

The main goal of this thesis is to study the effect of temperature on the electrochemical CO_2 reduction. We start this study at ambient pressures on several different heterogeneous electrocatalysts. Simultaneously, we have developed a high-pressure, high-temperature electrochemical setup which allows us to study the effect of temperature at elevated pressures, which is discussed in the second part of this thesis.

Chapter 2 discusses the effect of temperature on the CO2RR on Au using a rotating-ring disk electrode (RRDE) system. Au was chosen as first electrocatalyst to study as it is a relatively simple system which produces only CO and H_2. We show that temperature can enhance both the activity and selectivity for the CO2RR although an optimum is observed at intermediate temperature (ca. 50 °C) and at high temperatures the selectivity decreases again. In **Chapter 3**, we move on to a more complex catalyst namely Cu. Cu produces a great variety of CO2RR products, the formation of which behave differently with temperature. Methane and formate selectivity decrease with temperature, while ethylene and ethanol show an optimum around 48 °C. This optimum divides the temperature effect in two regimes. In the first regime up to 48 °C, C2+ activity and selectivity increases with temperature and HER selectivity remains stable. We contribute this to a combination of kinetics, local pH and CO coverage. In the second regime after 48 °C, C2+ selectivity decreases and HER starts to dominate. This is contributed to a too high local pH in combination with a changing Cu surface. In **Chapter 4** we try to improve the Cu catalyst at high temperatures and inhibit HER by alloying Cu with Ag. We show that HER can indeed be inhibited at high temperatures, although the optimum in C2+ products is still observed. Moreover, we study the effect of temperature on Ag itself and compare this to results of Au from Chapter 2. We observe that mass transport and the applied potential are important other parameters influencing the temperature effect, which is also convoluted with the effect of CO_2 solubility.

Chapter 5 studies the electrochemical CO2 reduction on Ni. Even though Ni is not a very active CO2RR catalyst, it is interesting to study as it makes C-C bonds via a chain-growth mechanism, in contrast to the CO dimerization mechanism on Cu. We show the effect of temperature, partial pressure, potential and electrolyte composition on the activity and chain-growth probability.

Chapter 6 discusses the development of the high-pressure, high-temperature setup. As a proof of concept, we show the effect of temperature and pressure on the CO2RR on Au. At ambient pressures similar results are obtained as in Chapter 2, but at higher pressures the optimum in FE towards CO with temperature vanishes. Temperature and pressure then have no significant effect on the selectivity anymore, but still enhance the activity significantly. **Chapter 7** follows the sequence of the beginning of the thesis where a study using Au electrodes is followed by a study using Cu electrodes. We show that temperature influences the selectivity more significantly than pressure. Most interestingly, at very high temperatures, above 100 °C, the C-C coupling mechanism changes from the CO dimerization mechanism to the chain-growth mechanism observed for Ni in Chapter 5. Moreover, we show that elevated CO_2 pressures can stabilize the Cu and increase the temperature range in which high C2+ selectivity can be reached in the dimerization mechanism.

The electrode categorization discussed in section 1.3 is based on experiments at ambient temperatures. To see if this categorization is still valid and to observe the effect of pressure and temperature on the CO2RR on various electrodes, we performed a catalyst screening study in **Chapter 8**, where we study 20 metals at elevated temperatures and pressures. We show that elevated pressures inhibit HER significantly and turn reasonable CO2RR catalysts into excellent catalysts with more than 90% FE for CO2RR, which can be maintained even at 100 °C. However, when a catalyst produces mostly H_2 at ambient conditions, it does not become a good catalyst at elevated pressures, although some metals can produce interesting products such as methanol and long chain hydrocarbons, but in (very) low quantities.

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