Selectivity and competition between the anodic evolution of oxygen and chlorine

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INTRODUCTION

1.1. Electrochemistry at the center of future energy

Humanity faces important environmental challenges in the coming century. The most pressing of these issues is by far the global rise in CO_2 emissions, which has significantly disbalanced the earth's natural carbon cycle since the start of the industrial revolution.[1] To prevent climate change, which may have highly detrimental consequences for humanity's prosperity, the world economy will have to make significant changes in its energy infrastructure.

The issue of carbon-induced climate change is intimately coupled to a more general one, which is the source of energy used for driving human enterprise. Since the industrial revolution, humanity has been almost exclusively dependent on the burning of fossil fuels for its energy needs and economic development.[2] Besides their environmental impact, fossil fuels are inherently constrained by political instability, as well as ultimately by their limited supply.[3]

The most compelling alternative to fossil fuels is solar energy, where radiation emitted by the sun may be captured using photovoltaics.[4] This leads to the direct generation of electricity, which is the most useful form of energy. This generated electricity can facilitate virtually every function that fossil fuels serve present day, and it is essentially an endless source of energy since the sun is eternal within a human lifetime.[5–7]

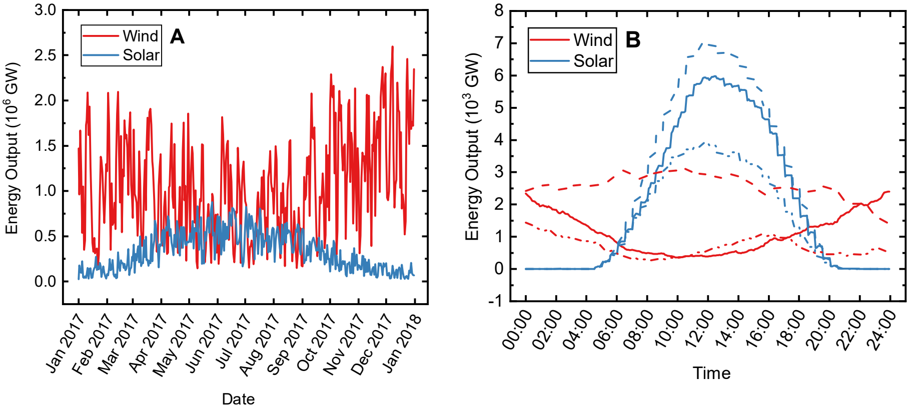

Figure 1.1: Power output data of the UK power grid, showing wind and solar, during the year 2017 (A), as well as three consecutive days around the end of May, 2017 (B). Data downloaded from https://gridwatch.co.uk/, October 2018.

Electrical energy can be involved in inducing chemical transformations; this is the domain of electrochemistry.[8] Electrochemical reactions can play a key role in rebalancing the world's carbon footprint, which requires that the net emission of carbon into the atmosphere must be reduced. Instead of burning fossil fuels and harnessing the resulting heat and gas expansion work, energy from the sun is converted to electrical energy which can then be coupled to the making and breaking of chemical bonds. An electrochemistry-facilitated method for harnessing solar energy that especially appeals to the imagination is water electrolysis coupled to fuel cells, where hydrogen (H_2) is used as energy carrier.[9–11] Only water, H_2 gas and oxygen gas (O_2) are involved as chemicals, making the overall process extremely environmentally friendly. In effect, one can use it to power a car or any other electrical device with nothing but solar energy and water. The process can serve as a means to capture and store energy from solar power and other renewables. This is direly needed, since photovoltaic devices and wind turbines, which are the primary sources of renewable electricity, have a highly intermittent output (see Figure 1.1).[12–14]

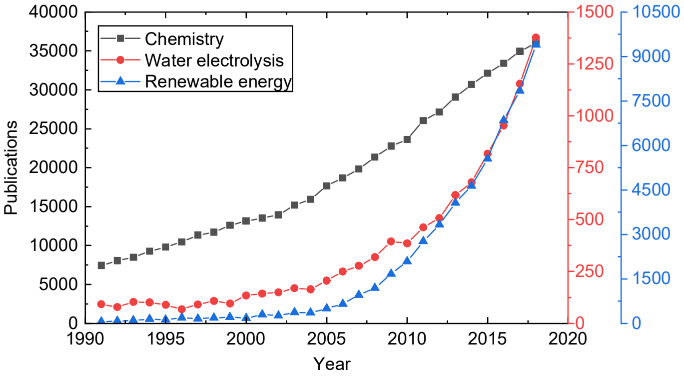

Figure 1.2: Publications since 1990 related to topics "Water electrolysis" and "Renewable energy", compared to publication output related to the more general term "Chemistry". Data downloaded from Web of Science (webofknowledge.com), September 2019.

Electrochemical processes related to energy storage have always been associated with high capital costs due to the price of electricity and the necessary electrolyzer designs.[15,16] Additionally, the most attractive of these processes are plagued by energy efficiency problems that have yet to be resolved. In case of the aforementioned combination of water electrolysis and fuel cells, these issues are caused in large part by the slow reactivity of O_2-related reactions.[17–20] They will be discussed in more detail throughout this thesis.

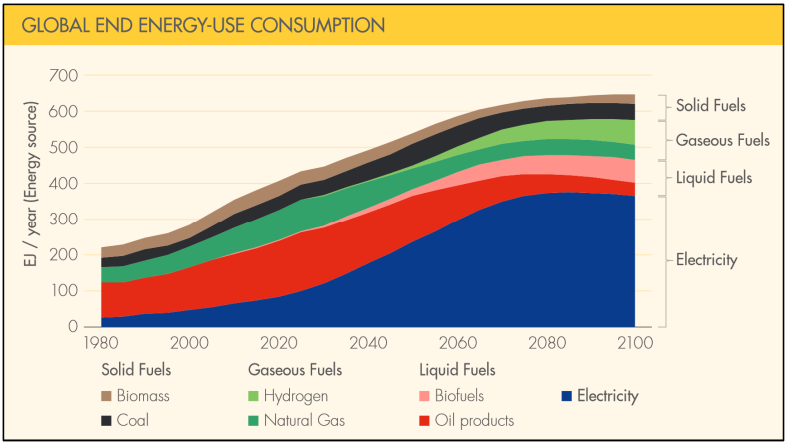

Figure 1.3: Predicted distribution of world-wide energy consumption up until 2100. Image and data by Shell, from Shell Sky Scenario (October 2018).

Fortunately, the research interest in electrochemistry and sustainable energy research has increased significantly in recent years (Figure 1.2); this trend has been driven in part by increasing public awareness of climate change and the recent Paris climate agreement.[21] Electrochemistry will play an increasingly important role in the decades to come as the world energy infrastructure becomes more and more electrified (Figure 1.3).

1.2. Water electrolysis and the oxidation of chloride

As mentioned in section 1.1, electrical energy can be used in an electrolyzer that generates H_2 on the cathode and O_2 on the anode, splitting water according to:

$$2\ H_2O \rightarrow 2\ H_2 + O_2 \qquad \text{Eq. 1.1}$$

The H_2 produced according to Eq. 1.1 can be said to contain the energy input that was used to drive the reaction. It can be stored, transported and used as feedstock in a fuel cell where it is recombined with atmospheric O_2 to form water. This route of energy capture, storage and utilization avoids the burning of fossil fuels if electricity generated by renewables is used. Moreover, it then has zero net-emission of CO_2 and does not involve environmental pollutants in any of its stages. The overall splitting reaction proceeds as two half-reactions within the electrolyzer, where H_2 is produced by the reduction of protons in the aqueous solution:

$$2\ H^+ + 2\ e^- \rightarrow H_2 \qquad \text{Eq. 1.2}$$

$$E^0_{H^+/H_2} = 0\ \text{V vs. RHE}$$

Another promising electrochemical approach for achieving zero net-carbon emissions is to capture CO_2 at emission hotspots and convert it to useful starting materials. Instead of directly targeting protons, the cathodic reaction is then the reduction of CO_2, which can lead to a wide range of useful products, such as methanol, ethylene, or CO (shown below):[22–24]

$$CO_2 + 2\ H^+ + 2\ e^- \rightarrow CO + H_2O \qquad \text{Eq. 1.3}$$

$$E^0_{CO_2/CO} = -0.11\ \text{V vs. RHE}$$

Regardless of the reduction reaction, it must always be coupled to an oxidation reaction to complete the electrochemical device. This reaction can be the oxidation of water to form oxygen (O_2), which is essentially a by-product:

$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^- \qquad \text{Eq. 1.4}$$

$$E^0_{O_2/H_2O} = 1.229\ \text{V vs. RHE}$$

Eq. 1.4 is known as the Oxygen Evolution Reaction (OER). It is a highly desirable counter reaction because water as a reactant is readily available on earth, and O_2 is environmentally harmless, meaning that it can be safely released into the atmosphere.

It must be noted that industrial-scale electrolysis would require large amounts of water as feedstock. However, freshwater on earth is a precious and scarce commodity. Furthermore, areas where the influx of renewable energy from wind and solar are the highest, are often at or near the sea.[25–27] Seawater, which is also vastly more earth-abundant than freshwater, would thus be a much better substrate for use in large-scale electrolysis.[25,27,28] The original idea of a 'hydrogen economy', as first proposed by Bockris in the 1970s, was in fact based on the direct electrochemical splitting of seawater using nuclear or solar power near arid sea coasts, where the influx of solar energy is high and reliable.[9,26] Saline water, which contains high concentrations of chloride ions (~0.6 M), unfortunately raises a major challenge when used as substrate in an electrolyzer; in chloride solutions, Cl^- may oxidize to form labile and powerful oxidizing agents, such as chlorine gas (Cl_2).[29–32] Contrary to O_2, such species cannot be easily disposed of in an environmentally friendly way, and the rate of their formation usually dwarfs the rate of the OER, as will be discussed in more detail below.

The reaction where Cl_2 is formed directly from Cl^- is termed the Chlorine Evolution Reaction (CER). The CER is highly unwanted in electrolyzers where only the cathodic reaction is of interest, such as for renewable energy storage. There are however several areas of industry where chloride oxidation is a reaction of great importance, such as the chlor-alkali process.[33–35] The CER is the desired anodic reaction in this process, where brine (concentrated NaCl) is electrolyzed according to:

$$2\,H_2O + 2\,Na^+ + 2\,Cl^- \rightarrow H_2 + Cl_2 + 2\,Na^+ + 2\,OH^- \qquad \text{Eq. 1.5}$$

The jointly generated Cl_2 and NaOH are bulk chemicals that underpin approximately 50% of the global chemical industry.[36–39] The chlor-alkali process is very energy intensive; the required power input to drive chlorine formation is the most significant economic (and environmental) cost.[33,40–42] In 2006 the process consumed approximately 334 PJ of electrical energy in the U.S. alone.[43] A substantial body of research has thus gone in studying optimum process conditions for the CER, since the large scale of the process means that even small efficiency gains can have a large impact.[34,44,45] In this regard, the OER is highly unwanted in the chlor-alkali process; the formation of O_2 not only compromises the overall process efficiency and catalyst stability, but also represents a safety risk.[34,35,46–48] Competition between the OER and CER is also relevant to electrochemical water treatment, where strongly oxidizing 'active chlorine' may be electrochemically generated to eliminate pollutants.[49–51] However, its formation has to be tightly controlled or is sometimes unwanted.[52,53] Finally, the OER is usually the sole desired counter reaction in electrowinning, where the electrolysis bath often contains traces of chloride.[54] The OER and CER thus both lie at the heart of large-scale electricity-to-chemical conversion steps, which makes them highly important to a renewable-based energy infrastructure.

Both the OER and CER have been the subject of intense study over the past five decades, with significant improvements in catalyst performance for both of them.[33] They are most readily catalyzed on metal oxides.[55–57] The CER is usually carried out in acidic media because of thermodynamic restrictions (see section 1.3), on anodes made of mixtures of RuO_2 and TiO_2, so-called Dimensionally Stable Anodes (DSA®).[33] Pt is also known to catalyze the CER at high intrinsic rates, but suffers from inhibition due to transient formation of platinum oxides (see Chapter 4).[58] The OER can be carried out in a wide pH range, but performance wise, the current state of the art is represented by polymer electrolyte membrane (PEM) electrolyzers which employ acidic pH and are equipped with Ir-based mixed metal oxides.[59] Unfortunately, Ir is a highly scarce, expensive material, and the strong reliance of acidic PEM electrolyzers on Ir forms a severe bottleneck against wide-spread implementation. Major research effort is currently being devoted to finding alternatives that are stable and OER-active in an acidic environment without relying on rare precious metals.[60–62]

1.3. Kinetics and competition of the OER and CER

The oxidation of $\mathrm{Cl^-}$ in aqueous media can lead to a variety of products. In acidic media, the CER is the thermodynamically preferred reaction, which can be written as:

$$2\ \mathrm{Cl^-} \rightarrow \mathrm{Cl_2} + 2\ \mathrm{e^-} \qquad \text{Eq. 1.6}$$

$$E^0_{Cl_2/Cl^-} = (1.358 + 0.059\mathrm{pH})\ \mathrm{V\ vs.RHE}$$

In acidic aqueous solution, the CER has an equilibrium potential that is close to the OER (Eq. 1.4), and will therefore be a competing reaction. The OER is a notoriously slow reaction for which no perfect catalyst has been found yet, despite enormous research efforts. Its difficult kinetics lead to a significant overpotential (typically between 0.25 - 0.35 V) and corresponding energy losses. This is one of the reasons that large-scale energy storage by means of water electrolysis has not yet been realized.[20,63–66] The difficulty of catalyzing the OER lies in its four-electron nature, which implicates a complex reaction pathway involving a minimum of three or even four intermediates.[64,67,68] The CER on the other hand involves the transfer of only two electrons and presumably only a single catalytic intermediate, therefore it is intrinsically a much faster reaction.[68] It was previously estimated that the CER exchange current density is 4-7 orders of magnitude higher than that of the OER.[25] For a pH of around 1-2, this leads to the situation that $\mathrm{Cl_2}$ can be evolved exclusively, despite the thermodynamic preference for the OER. In fact, the facile CER kinetics relative to the OER is what makes it possible to vigorously evolve chlorine in acidic aqueous media during the chlor-alkali process, with minimal anodic decomposition of the aqueous solvent.

Note that the equilibrium potential for the OER is pH-dependent, and therefore pH-independent on the reversible hydrogen electrode (RHE) scale, whereas the reverse is true for the CER. The selectivity between the OER and oxidation of chloride is thus expected to shift with differences in bulk acidity. As the solution pH increases, there is an increasing thermodynamic preference towards the formation of hypochlorous acid or hypochlorite:[29]

$$\mathrm{Cl^-} + \mathrm{H_2O} \rightarrow \mathrm{HClO} + \mathrm{H^+} + 2\ \mathrm{e^-} \qquad \text{Eq. 1.7}$$

$$E^0_{HClO/Cl^-} = (1.482 + 0.030\mathrm{pH})\ \mathrm{V\ vs.RHE}$$

$$\mathrm{Cl^-} + \mathrm{H_2O} \rightarrow \mathrm{ClO^-} + 2\ \mathrm{H^+} + 2\ \mathrm{e^-} \qquad \text{Eq. 1.8}$$

$$E^0_{ClO^-/Cl^-} = 1.636\ \mathrm{V\ vs.\ RHE}$$

These reactions come into play because higher pH favors the disproportionation of $\mathrm{Cl_2}$ into HClO and $\mathrm{ClO^-}$, according to:

$$\mathrm{Cl_2(aq) + H_2O \rightleftharpoons HClO(aq) + H^+ + Cl^-} \qquad \text{Eq. 1.9}$$

$$\mathrm{pK}_a = 2.98$$

$$\mathrm{HClO(aq) \rightleftharpoons H^+ + ClO^-} \qquad \text{Eq. 1.10}$$

$$\mathrm{pK}_a = 7.53$$

From Eq. 1.9 and Eq. 1.10, the reactions in Eq. 1.7 and Eq. 1.8 have equilibrium potentials equivalent to the CER at $\mathrm{pH} \approx 4$ and $\mathrm{pH} \approx 4.7$, respectively. The extent to which these reactions compete with the CER has never been investigated, since the rapid disproportionation of $\mathrm{Cl_2}$ in alkaline media makes it difficult to quantify them. We will offer an indirect indication of their occurrence based on arguments and data from sections 2.3.1 and 8.3.2. The CER is by far the most studied reaction, as it is the most relevant industrially (see section 1.2). At pH values higher than 7, the competition between this reaction and the OER becomes dictated by thermodynamics. While this is a useful practical approach for enhancing OER selectivity over the oxidation of chloride, it prohibits an in-depth investigation in how the reactions interact mechanistically.

Although the OER and CER look like fundamentally different reactions at first glance, it has often been observed that their activities are coupled; catalyst materials proficient at the OER are often also highly active for the CER.[55,69–71] This implies that the two reactions have a similar active site, or partially shared reaction pathways. It also suggests that the key intermediates related to oxygen and chlorine have similar binding modes on OER catalysts. This leads to a so-called scaling relationship between them, as has been suggested by recent work using Density Functional Theory (DFT) to study possible kinetic mechanisms of the OER and CER.[72–77] Existence of such a scaling implies that control over selectivity between the two reactions can be a serious challenge. It may be difficult, if not impossible, to efficiently separate the two reactions on the basis of kinetic considerations alone, such as by finding an appropriate catalyst.[71,78,79]

The OER is usually accompanied by catalyst degradation, which is a major problem for the durability of practical electrolyzers.[80–82] For pure metal oxides, the OER activity and extent of catalyst degradation have been directly correlated,[81,83] implying an additional 'scaling relation' between the evolution of $\mathrm{O_2}$ and some catalyst dissolution pathway.[84] However, it has also been reported that OER activity and catalyst degradation can be decoupled, such as by mixing with appropriate heterometal oxides.[85,86] The CER also seems to correlate with catalyst degradation, but not in the same way that the OER does.[87–90]

1.4. Review of microkinetic models

The OER is a highly complex reaction that proceeds through at least three reaction intermediates, which can be written schematically as S-OH, S=O and S-O-OH, where S denotes a surface site on the catalyst.[91–93] There is involvement of multiple intermediates simultaneously adsorbed on the surface, and the reaction pathway may also diverge; O-O bond formation may take place through the conversion of the 'oxo' intermediate S=O into the 'peroxo' intermediate S-O-OH, or through a (non-electrochemical) recombination of two oxo-intermediates.[94–97] Mars-van Krevelen type behavior, where lattice oxygen in the catalyst surface itself actively participates and reconstructs during the reaction, has been repeatedly observed,[65,98–100] as well as a dependency of the apparent OER kinetics on gas transport and the porosity of the used catalyst.[101–104] The OER is thus best studied on simplified, non-porous model surfaces (such as single crystals),[105–107] which falls outside the scope of this thesis. We will therefore mostly refrain from modelling kinetic parameters measured during the evolution of oxygen.

In contrast to the OER, a microkinetic model of the CER is more straightforward, because the reaction involves the transfer of only two electrons. In the following, we will discuss kinetic models for the CER, summarizing from existing literature.[35,108–113] This discussion is also relevant to other two-step mechanisms involving two electrons, such as the evolution of bromine or hydrogen. In the literature, the first step towards the formation of $\mathrm{Cl_2}$ is typically assumed to be the fast adsorption and discharge of a chloride atom on the catalyst surface, termed the Volmer step (Eq. 1.11):

$$\mathrm{Cl^-} + * \rightleftarrows \mathrm{Cl^*} + \mathrm{e^-} \qquad \text{Eq. 1.11}$$

Here, $*$ represents a free catalytic site, and $\mathrm{Cl^*}$ is a reactive chlorine intermediate adsorbed on the surface. On metal oxide catalysts such as $\mathrm{RuO_2}$ and $\mathrm{IrO_2}$, the exact nature of $*$ and $\mathrm{Cl^*}$ in Eq. 1.11 has not been completely resolved. It is probably intricately coupled to the surface chemistry of the oxide, as the CER rate has been shown to be slowed down by $\mathrm{H^+}$ in very high concentrations.[35,56] Eq. 1.11 is thus likely a simplification, but the reaction it represents is not rate-limiting as long as extremely low pH (< 0) is avoided. The $\mathrm{Cl^*}$ surface coverage θ_{Cl} is then in quasi-equilibrium with the subsequent rate-limiting step, and can be written as a fraction (between 0 and 1) of the 'maximum coverage'. As a further approximation, one can assume that the adsorption of chloride obeys the Langmuir isotherm, based on the mean-field approximation.[114] The adsorption of $\mathrm{Cl^*}$ can then be described by:

$$\theta_{Cl} = \frac{K_{Cl}[\mathrm{Cl^-}]e^{f\eta}}{K_{Cl}[\mathrm{Cl^-}]e^{f\eta} + 1} \qquad \text{Eq. 1.12}$$

In Eq. 1.12, η is an overpotential defined as $\eta = E - E^0$, where E^0 can be the standard equilibrium potential of the overall reaction, or any other suitable reference potential. K_{Cl} is then the chloride adsorption constant at $\eta = 0$, $[\mathrm{Cl^-}]$ is the chloride concentration, and $f = F/(RT)$.

The Volmer discharge is thought to be followed by several different types of step, depending on the catalyst material and system conditions. In the Heyrovský step, the evolution of a Cl_2 molecule follows from an electron transfer reaction between Cl^* and a second Cl^- ion from solution, reminiscent of the Eley–Rideal mechanism in heterogeneous gas-phase reactions:

$$\mathrm{Cl}^* + \mathrm{Cl}^- \rightleftarrows \mathrm{Cl}_2 + \mathrm{e}^- + * \qquad \text{Eq. 1.13}$$

At overpotentials high enough that the backward reaction of Eq. 1.13 is negligible, the j vs. E relationship predicted by the Volmer-Heyrovský (V-H) mechanism can be written as:

$$j_{VH} = 2Fk_H\theta_{Cl}e^{\alpha_H f\eta}[\mathrm{Cl}^-] = 2Fk_H\frac{K_{Cl}[\mathrm{Cl}^-]^2e^{(\alpha_H+1)f\eta}}{K_{Cl}[\mathrm{Cl}^-]e^{f\eta}+1} \qquad \text{Eq. 1.14}$$

In the above, k_H is the rate constant of the Heyrovský reaction when $\eta = 0$, and α_H is the corresponding transfer coefficient. Alternatively, the Krishtalik mechanism assumes that desorption is a two-step process, involving a second type of chlorine intermediate:

$$\mathrm{Cl}^* \rightleftarrows \mathrm{Cl}^{*+} + \mathrm{e}^- \qquad \text{Eq. 1.15}$$

$$\mathrm{Cl}^{*+} + \mathrm{Cl}^- \rightleftarrows \mathrm{Cl}_2 + * \qquad \text{Eq. 1.16}$$

This mechanism is only expected to occur on metal oxides.[35] The electron transfer in Eq. 1.15 is assumed to be rate-limiting relative to the (non-electrochemical) desorption step in Eq. 1.16, where the rather exotic chloronium (Cl^{*+}) intermediate would be stabilized by the metal oxide surface, as its structure is usually proposed to be $(\mathrm{O}-\mathrm{Cl}^*)^+$. When again assuming that η is positive enough that the forward reaction dominates, Eq. 1.15 predicts that:

$$j_{VK} = 2Fk_K\theta_{Cl}e^{\alpha_K f\eta} = 2Fk_K\frac{K_{Cl}[\mathrm{Cl}^-]e^{(\alpha_K+1)f\eta}}{K_{Cl}[\mathrm{Cl}^-]e^{f\eta}+1} \qquad \text{Eq. 1.17}$$

where the symbols have similar meanings as in Eq. 1.14. The Volmer-Krishtalik (V-K) mechanism predicts the same functional j vs. E relationship as V-T, but it differs in its $[Cl^-]$ dependence.

Finally, a third type of rate-limiting step has also been described, similar to the Langmuir-Hinshelwood mechanism in gas-phase catalysis. It is termed the Tafel step:

$$2\,\mathrm{Cl}^* \rightarrow \mathrm{Cl}_2 + 2\,* \qquad \text{Eq. 1.18}$$

This mechanism assumes that the reaction is fully dependent on surface-bound species, and that the rate-limiting step is non-electrochemical. The Volmer-Tafel (V-T) mechanism implies that the forward current density follows:

$$j_{VT} = 2Fk_T(\theta_{Cl})^2 = 2Fk_T\left(\frac{K_{Cl}[\mathrm{Cl}^-]e^{f\eta}}{K_{Cl}[\mathrm{Cl}^-]e^{f\eta}+1}\right)^2 \qquad \text{Eq. 1.19}$$

where k_T is the non-electrochemical rate constant for Cl^* recombination. The Volmer-Tafel mechanism is dominant during the CER on Pt and is usually not considered on metal oxides.

The V-H, V-K and V-T mechanisms all make specific predictions about the observed kinetics of the CER. We will primarily consider Tafel slopes (b) and reaction orders ($\mathcal{R}$). These quantities, defined as $b = \partial\eta / \partial \log(\text{j})$ and $\mathcal{R} = \partial \ln(\text{j}) / \partial \ln([\text{Cl}^-])$, are easily accessible through experiment and in this way provide convenient diagnostic tools for the underlying mechanism. Their derivations are shown in Table 1.1, and some general limiting cases are summarized in Table 1.2. These values will be discussed frequently throughout Chapters 3, 4 and 5.

We note that Tafel analysis can prove very useful for kinetic investigations, but the 'meaning' of the slope can be obfuscated by a wide variety of phenomena.[109,115,116] There is also significant width and overlap of the predicted Tafel slopes between the various mechanisms. One must thus exert caution when using Tafel values as a comprehensive diagnosis of the 'real mechanism'. One of the key points of Table 1.1 is that reaction orders and Tafel slopes of reactions involving a chemisorbed intermediate are never expected to remain constant as function of potential or concentration in the bulk, because of varying surface coverage of the intermediate. This has been comprehensively described by Conway and co-workers,[112] and more recently by Rosestolato and co-workers.[117]

Table 1.1: Theoretical Tafel slopes and reaction orders for two-step reaction mechanisms for the CER, under the assumption that $\alpha_H = \alpha_K$.

	Volmer-Heyrovský	**Volmer-Krishtalik**
Tafel slope $b = \left(\frac{\partial \log j}{\partial \eta}\right)^{-1}$	$\frac{\ln(10)}{f}\left(\frac{K_{Cl}[\text{Cl}^-]e^{f\eta}+1}{\alpha_H(K_{Cl}[\text{Cl}^-]e^{f\eta}+1)+1}\right)$	Same as Volmer-Heyrovský
Cl^- reaction order $\mathcal{R}_{\text{Cl}^-} = \frac{\partial \ln j}{\partial \ln[\text{Cl}^-]}$	$2-\theta_{Cl}$ $= \frac{K_{Cl}[\text{Cl}^-]e^{f\eta}+2}{K_{Cl}[\text{Cl}^-]e^{f\eta}+1}$	$1-\theta_{Cl}$ $= \frac{1}{K_{Cl}[\text{Cl}^-]e^{f\eta}+1}$
	Volmer-Tafel	
Tafel slope $b = \left(\frac{\partial \log j}{\partial \eta}\right)^{-1}$	$\frac{\ln(10)}{2f}\frac{1}{(1-\theta_{Cl})}$ $= \frac{1}{2f\log(e)}(K_{Cl}[\text{Cl}^-]e^{f\eta}+1)$	
Cl^- reaction order $\mathcal{R}_{\text{Cl}^-} = \frac{\partial \ln j}{\partial \ln[\text{Cl}^-]}$	$2(1-\theta_{Cl})$ $= 2\left(\frac{1}{K_{Cl}[\text{Cl}^-]e^{f\eta}+1}\right)$	

Table 1.2: Cases of limiting behavior for two-step reaction mechanisms for the CER. Data is shown as function of the overpotential η *and 'chloride adsorption strength'* $K_{Cl}[Cl^-]$. *It was assumed that* $\alpha_H = \alpha_K = 0.5$.

Limiting case		**Volmer-Heyrovský**	**Volmer-Krishtalik**
Tafel slope b	$\eta \to 0$	$b \approx 40\ \mathrm{mV\ dec^{-1}}$ if $K_{Cl}[\mathrm{Cl^-}] \approx 0$ $b \to 120\ \mathrm{mV\ dec^{-1}}$ if $K_{Cl}[\mathrm{Cl^-}] \to \infty$	Same as Volmer-Heyrovský
	$\eta \to \infty$	$b \to 120\ \mathrm{mV\ dec^{-1}}$	
$\mathrm{Cl^-}$ reaction order $\mathcal{R}_{\mathrm{Cl^-}}$	$\eta \to 0$	$\mathcal{R}_{\mathrm{Cl^-}} \approx 2$ if $K_{Cl}[\mathrm{Cl^-}] \approx 0$ $\mathcal{R}_{\mathrm{Cl^-}} \to 1$ if $K_{Cl}[\mathrm{Cl^-}] \to \infty$	$\mathcal{R}_{\mathrm{Cl^-}} \approx 1$ if $K_{Cl}[\mathrm{Cl^-}] \approx 0$ $\mathcal{R}_{\mathrm{Cl^-}} \to 0$ if $K_{Cl}[\mathrm{Cl^-}] \to \infty$
	$\eta \to \infty$	$\mathcal{R}_{\mathrm{Cl^-}} \to 1$	$\mathcal{R}_{\mathrm{Cl^-}} \to 0$

Limiting case		**Volmer-Tafel**
Tafel slope b	$\eta \to 0$	$b \approx 30\ \mathrm{mV\ dec^{-1}}$ if $K_{Cl}[\mathrm{Cl^-}] \approx 0$ $b \to \infty$ if $K_{Cl}[\mathrm{Cl^-}] \to \infty$
	$\eta \to \infty$	$b \to \infty$
$\mathrm{Cl^-}$ reaction order $\mathcal{R}_{\mathrm{Cl^-}}$	$\eta \to 0$	$\mathcal{R}_{\mathrm{Cl^-}} \approx 2$ if $K_{Cl}[\mathrm{Cl^-}] \approx 0$ $\mathcal{R}_{\mathrm{Cl^-}} \to 0$ if $K_{Cl}[\mathrm{Cl^-}] \to \infty$
	$\eta \to \infty$	$\mathcal{R}_{\mathrm{Cl^-}} \to 0$

The above models all make use of a Langmuir model isotherm for chloride adsorption. In reality, repulsive interactions between adsorbed chloride (and halides in general) will exist.[114] If this is taken into account by using a Frumkin isotherm, this will lead to a broadening of the isotherm, i.e. a broader range of chloride concentrations or potential is needed to reach maximum coverage. For the models described above, this implies that the basic predictions remain the same, but the range of chloride concentrations and potential where changes are observed will widen.

1.5. Previous literature and the outline of this thesis

The encompassing goal of the work in this thesis is to deepen the understanding of the OER and CER, in the context of the two gas-evolving reactions taking place simultaneously on a catalyst surface. The central question is selectivity and the interplay between the reactions, and how these relate to mutual kinetic competition. There is almost no situation imaginable where the formation of a mixture of $\mathrm{O_2}$ and $\mathrm{Cl_2}$ is an attractive outcome; the 'perfect selectivities' would be 100% or 0% of either species evolved.

Of special interest are anodes that evolve oxygen exclusively during seawater splitting, as these would be highly valued, but due to the OER's kinetic disadvantage, also by far the most challenging to develop. A large body of research concerning the OER has been published, but the majority concerns electrolytes that are free of chloride. Interest in saline water splitting is relatively sparse, although there has been an increase recently.

On the other hand, the perspective of CER research is dominated by the chlor-alkali industry. Most CER papers are restricted to concentrated chloride solutions (1 M or higher) and high current densities comparable to industrial operation, as well as DSA®-based industrial model catalysts, which have relatively poorly defined surfaces. The OER is usually only considered for its effect on catalyst stability; its selectivity during the CER is ignored. Outside of some work in electrochemical water treatment, behavior of the CER from relatively dilute chloride solutions (< 100 mM) has seen little attention, even though this limiting region may contain especially relevant details concerning its mechanism and the effect on the OER.

This thesis is thus specifically focused on the selectivity between the CER and OER in such dilute acidic chloride solutions, where the OER and CER have comparable onset potentials and current densities, and are in direct kinetic competition. By studying multiple reactions simultaneously, 'cross-linked' insights may be obtained, deepening the understanding of the OER as well as the CER. This may aid the development of better catalytic materials for both. Chapter 2 describes a new method for measuring CER selectivities in relevant dilute chloride solutions, which enables rapid and accurate screening of OER vs. CER behavior over a wide potential range. Chapter 3 looks deeper into the coupling between OER and CER activity on a series of closely related Ir-based double perovskite electrocatalysts, and how the oxidation of water and chloride affect their stability. Chapters 4 and 5 investigate the parallel oxidation of chloride, bromide and water. As seawater contains a small fraction of bromide in addition to chloride, these systems would better resemble the situation in an actual electrolyzer. Close attention is paid to how bromide and its oxidation affects both the CER and OER. Chapters 6 and 7 focus on OER-selective anodes. Chapter 6 investigates the origin of manganese oxide-based anodes, and their unusual preference for evolving oxygen. We find that the manganese oxide overlayer actually induces the selectivity by forming an electrochemically inert barrier, that prevents Cl^- from reacting. This represents a highly promising method for decreasing CER selectivity, which is explored further in Chapter 7. Finally, Chapter 8 documents pitfalls for quantifying gas-evolving reactions on a rotating ring-disk electrode, which were often encountered during experiments throughout this thesis. Possible solutions are offered to increase the gas collection reliability. Chapter 9 contains all supporting information, ordered in subsections according to the corresponding chapter numbers.