Intrinsic Catalytic Properties of Electro catalysts, 
a Model Surface Approach

Dissertation

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**List of abbreviations**

PEM = Proton Exchange Membrane
ODC = Oxygen depolarized cathode
CER = Chlorine evolution reaction
OER = Oxygen evolution reaction
HER = Hydrogen evolution reaction
ORR = Oxygen reduction reaction
$\Delta G$ = free energy change
$j_0$ = exchange current density
$V$ = volt
LIPT = laser-induced potential transient
PME = potential of maximum entropy
$E_{PZC}$ = potential of zero charge
$E_{PZTC}$ = potential of zero total charge
$E_{PZFC}$ = potential of zero free charge
$\Phi^M$ = work function
$j$ = current density
$v$ = electrochemical reaction rate
$D$ = diffusion coefficient
$C$ = concentration
$C_s$ = concentration at the surface
$j_{act}$ = activation current density
$j_{meas}$ = measured current density
$j_{ms}$ = mass transport current density
$j_{limited}$ = mass-transport limited current density
$Z(\omega)$ = impedance of the system
$F$ = Faraday constant
$\omega$ = angular frequency
$E$ = potential
RHE = reversible hydrogen electrode
$f$ = frequency
$t$ = time
$\Phi$ = phaseshift
UME = ultra-microelectrode
$r_0$ = radius
RDE = rotating disk electrode
RRDE = rotating ring disk electrode
$\mu$m = micro-meter
$\alpha$ = thermal diffusivity of the solution
t = time
s = second
ΔT = change in temperature
C = Coulomb
S = entropy
δ = double layer length
EIS = electrochemical impedance spectroscopy
R = resistance
C = capacitance
$C_{DL}$ = double layer capacitance
$R_u$ = uncompensated resistance
EEC = equivalent electrical circuit
Hz = Hertz
OCP = open circuit potential
$R_b$ = electrolyte resistance in the presence of the non-conducting gas phase,
$R_e$ = electrolyte resistance without the gas phase
ε = gas phase fraction
e = electronic charge
q = charge
$\delta \chi^M_s$ = change in the surface electronic contribution to $\Phi^M$ caused by contact with solvent
g*(dip) = surface potential component due to net solvent dipole orientation
g_s^M(ion) = is the contribution from “free” charges to the surface potential component
$E_{abs(ref)}$ = “absolute” potential of the reference electrode.
Σ = charge situated on the metallic side of the double layer (so called free charge density)
$\Gamma_H$ = thermodynamic excesses of adsorbed hydrogen
$\Gamma_{OH}$ = thermodynamic excesses of adsorbed OH
RME = rotating microelectrode
t_i, = transport number of ion i
z_i = charge of the ion i
t_i = transport number of the ion i
$S_i$ = Eastman entropy of transport of the ion i
AFM = atomic force microscopy
STM = scannel tunneling microscopy
AIROF = anodically formed Ir oxide films
1. Introduction

The global energy consumption is expected to increase steadily in the next decades due to the higher living standards and the increasing population. A rising energy consumption increase the level of greenhouse gas emission which represents a serious threat to our planet. The increasing energy demand requires the development of renewable energy sources and a more efficient use of the industrial processes. Energy sources like wind and solar have a great potential, but their utilization is hindered by their intermittent nature [1]. When there is a fluctuation in the energy production, the energy supply is balanced by conventional power generation. For this reason, renewables would necessitate improved energy storage. Whereas batteries or capacitors are suited for the short-term storage of electricity, long-term storage could be realized with hydrogen as an energy carrier. The electricity generated by renewable energy sources can be converted into hydrogen by water electrolysis. The hydrogen thus produced can then be stored in pressure tanks and reconverted into electricity with fuel cells or hydrogen combustion engines.

The chemical industry and the scientific community are thus facing new challenges to accomplish the goal of a hydrogen-based economy. Electrochemistry has gained a special growth after the identification of these challenges. Further development of the electrocatalysis field in particular, appears necessary as the development of new processes and catalysts is required in order to fulfil the future environmental tasks, as well as the reduction of energy consumption in existing technologies. Among the key industrial processes in the field of electrocatalysis is the chlor-alkali production, whose yearly electricity demand alone is about 150 TWh [2]. Therefore, improvements in energy efficiency of this process could yield significant reductions in world energy consumption.
2. State-of-the-art

2.1 Hydrogen as energy carrier

Hydrogen may play an important role as an energy carrier of the future, as it can be used as fuel in almost every application where fossil fuels are being used today, but without polluting the environment. Hydrogen does not occur in nature in its elemental or molecular form, thus it has to be produced. On our planet the most abundant source of hydrogen is water, from which it can be obtained via water splitting. Thermodynamics asserts that water splitting is a demanding reaction, requiring more energy than the amount released from the produced hydrogen. Because of that, hydrogen is considered as an energy carrier, a convenient form of energy that can be stored and used when needed. Water electrolysis is a mature technology which can produce hydrogen with very high purity (up to 99.999%).

2.2 State of the art of electrolyzer technology

Most of electrolyzers used nowadays are based on alkaline electrolysis, but a consistent segment of the market is occupied by Proton Exchange Membrane (PEM) electrolyzers, which operate in acidic environment. In Figure 1A and B, schematic drawings of an alkaline and a PEM electrolyzer are depicted, respectively.

Figure 1: Schematic representation of (A) alkaline electrolyzer and (B) PEM electrolyzer. Adapted from [3].
Alkaline electrolysis is the most mature and understood technology for water splitting, being commercially available since decades [4]. Alkaline electrolyzers are the cheapest technology available since it is based on low-cost materials, such as nickel for both anode and cathode [5]. They operate in a highly corrosive environment, using concentrated KOH or NaOH electrolytes (NaOH and KOH between 20 – 30 wt.%) [6]. For this reason, the maintenance costs are very high and stack renovations are necessary every 8-12 years [7]. Therefore, finding new low cost electrode materials that are both efficient and durable is one of the challenges for the advance of alkaline water electrolysis. Another issue for the alkaline electrolyzers is their operative capabilities in transient conditions, which leads to problems because the electrolyzers have to be shut down when the input power is lower than the operational range (normally 25–50% of its rated capacity) [8, 9]. This is especially a relevant issue when the electrolyzer is connected with fluctuating renewable power sources, e.g. wind [9] or solar [10].

In a PEM electrolyzer, whose schematic representation is depicted in Figure 1B, water is fed to the anode, where oxygen gas and protons are formed. The generated protons migrate through the proton exchange membrane and reach the cathode, where they are reduced and form gaseous H₂. The voltage efficiency of PEM electrolyzers is between 67-82% [11] and their technology is still dependent on Ir at the anode and Pt at the cathode, being the two most efficient catalyst available in acidic condition. The state-of-the-art proton exchange membrane is a perfluorosulfonic acid polymer, known as Nafion™, which is also used in fuel cell technologies. The main challenge to be solved in order to improve this technology is the reduction of the catalyst loading, and the increase of its utilization and durability. Moreover, the understanding of the catalysts relation with the cell components could lead to an improving of the catalysts activity, thus increasing the electrolyzer performances.

In Table 1 the main aspects of both alkaline and PEM electrolyzers are summarized.
Table 1: Summary of the key operational parameters of alkaline and PEM electrolyzers.

<table>
<thead>
<tr>
<th></th>
<th>Alkaline electrolysis</th>
<th>PEM electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td>Available for large plant sizes, cost, lifetime [3, 12]</td>
<td>No corrosive substances, high power densities, high pressure &gt; 100 bar, dynamics [6, 13, 14]</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td>Low current densities, high maintenance costs (high corrosion due to strong alkaline solutions) [6, 14]</td>
<td>Expensive, fast degradation [14]</td>
</tr>
<tr>
<td><strong>Transient operation</strong></td>
<td>Possible, but lead to problems [8]</td>
<td>Better than alkaline electrolysis, dynamic adjustment possible [8]</td>
</tr>
<tr>
<td><strong>Duration</strong></td>
<td>Renovation stack: 8-12 years [7], lifetime: up to 30 years [6]</td>
<td>Lifetime: 5 years [8]</td>
</tr>
<tr>
<td><strong>System power</strong></td>
<td>4.7-5.4 [6]</td>
<td>5.2-7.1 [6]</td>
</tr>
<tr>
<td><strong>consumption (current) in kWh / m³ H₂</strong></td>
<td>4.5-7 [13]</td>
<td>4.5-7.5 [13]</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>60% - 71% [16]</td>
<td>65% - 83% [16]</td>
</tr>
</tbody>
</table>

As could be inferred by the discussion above, many issues need to be solved in order to enhance the performances for both systems. Among the challenges that need to be addressed to improve electrolysis technology, the pivotal one is the improvement of the materials in use. An advanced physical and electrochemical characterization of the catalysts, together with calculations to deeply understand the mechanism of the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), could be highly beneficial for the tailoring of the materials in use and could provide new guidelines for the discovery of most efficient catalysts.

### 2.3 State of the art of chlor-alkali electrolysis

Chlorine is one of the essential products of the chemical industry, with its annual production of 9,578 Ktons in 2015 in only Europe [17]. The two state-of the art technologies for the production of Cl₂ are chlor-alkali electrolysis using the membrane process and chlor-alkali electrolysis using oxygen depolarized cathodes (ODC). The membrane process is the most common in industry, while the ODC technology has been developed just in the last years and represents a marginal sector of the Cl₂ production [17].

In the membrane process, Cl₂ and NaOH are produced according to the following overall reaction:

\[
2 \text{NaCl} + 2 \text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2 \text{NaOH}
\]  
(Equation 1)
The overall reaction describing the chlor-alkali electrolysis using ODC is the following:

\[ 2 \text{NaCl} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cl}_2 + 2 \text{NaOH} \]  
(Equation 2)

A schematic representation of the two state-of-the-art technologies for the production of Cl\(_2\) is depicted in Figure 2.

![Diagram](image)

**Figure 2.** Schematic representation of: (A) the ODC chlor-alkali electrolysis and (B) the chlor-alkali membrane process. Adapted from [18].

The difference of these two processes consists in the reaction at the cathodic side, either the HER or the oxygen reduction reaction (ORR). The change from HER to ORR as cathodic reaction has been dictated by economical reason, since the overvoltage for the overall process decreases by about 1 V in the ODC technology, with a consequent energy saving of ~33% [19]. The electrolysis cells in both technologies are divided into two compartments by an ion-exchange membrane. The membrane separates the acidic brine at the anode side and the alkaline caustic soda solution at the cathode side and prevents the crossover of the produced gaseous products.

In the following work the scientific investigation is focused on the anodic reaction of the chlor-alkali electrolysis, namely the chlorine evolution reaction (CER). For the membrane-electrolysis the gas evolved at the anode is composed by [20]:

- \( \text{Cl}_2 \geq 98\% \) (vol)
- \( \text{O}_2 \approx 0.1-1.5\% \) (vol)
- \( \text{H}_2 < 0.05\% \) (vol)
The \( \text{H}_2 \) detected in the anode side is caused by the crossover from the cathode compartment and its percentage can be decreased via an improvement of the cell design and of the membrane. The presence of \( \text{O}_2 \) in the gas produced at the anodic side is caused by the parasitic OER reaction and it impacts significantly the costs of \( \text{Cl}_2 \) production. In fact, the chemical downstream processes using \( \text{Cl}_2 \) require an anhydrous, purified gas to get a high reliability and reduce the operating costs [21]. The process for the \( \text{O}_2 \) removal consists in a multi-step liquefaction process followed by the residual water vapor elimination via adsorption in concentrated sulfuric acid solution [22].

The increase of selectivity between \( \text{O}_2 \) and \( \text{Cl}_2 \) is therefore a fundamental issue in the chlor-alkali technology.

To get a complete picture of this issue, the anodic gas evolution has to be analyzed as a function of both the electrolyte and the anode composition, as well as other process conditions such as current density and temperature. For the improvement of the \( \text{Cl}_2 \) yield, all three aspects of the system need to be optimized: electrolyte contents, anode materials, and the process parameters. Research concerning the selectivity issue has been focused so far on the optimization of the anode material, but the precise tailoring of electrolyte components can affect the \( \text{O}_2/\text{Cl}_2 \) selectivity as well [23].

### 2.4 Electrocatalytic reactions

One of the main goal in the field of electrocatalysis research is the possibility of a quantitative prediction of a catalyst´s activity towards a certain reaction. In order to achieve this, description of the electrocatalytic system in kinetic terms is fundamental. The description, when accomplished, would permit rationalization of macroscopic trends in electrocatalysis. However, the characterization of an electrocatalytic system in kinetic terms is a demanding task.

The current approach to understand the kinetics is based on the transfer of properties at the atomic scale from the macroscopic system. The description of electrocatalytic systems is based on the use of “reaction descriptors”[24–26]. In these systems, the role of the catalyst is the stabilization of the reaction intermediates.

The pathway of a catalytic reaction is determined by the specific chemical interaction of the intermediates with the catalyst following the Sabatier principle. The Sabatier principle states that the reaction is hampered if the key catalytic intermediate interacts either too weak or too strong with the catalyst [27]. In the former case the reaction does not take place, in the latter the catalyst gets poisoned. The model to describe this interaction is based on the correlation between
energy of stabilization of the key catalytic intermediate and the activity towards a certain reaction. Thus, it is possible to understand and predict the activities of the catalyst semi-quantitatively by following the thermochemistry of the catalytic reaction. In fact, a catalytic reaction can be visualized in a form of free energy diagram, in which each step of the reaction requires a certain activation energy. The step of the reaction requiring the largest free energy is the “potential-determining step”. When a multiple-step reaction occurs, the key catalytic intermediate is the one involved in the reaction step with the largest free energy ($\Delta G$) [28].

With the application of this kinetic model, so-called volcano plots are constructed. Volcano-plots are widely used in electrocatalysis and have been adopted for the description of electrocatalytic reactions such as HER, CER and OER.

Along with the recent progress of computational chemistry, estimation of binding energies of reaction intermediates for HER, OER, and CER has facilitated the construction of volcano plots, casting further light into these reactions kinetics. Increasing effort from the scientific community has then been devoted to reach the tip of the volcano. The activity at the tip of the volcano can be achieved by optimization and improvement of existing materials and tailoring of the binding energies of the catalyst interface. The binding energies of a catalytic surface with intermediates are not exclusively determined by the intrinsic properties of the catalyst, but they are also influenced by the electrolyte components. As an example, the adsorption energies of the OER intermediates vary with temperature and pH value [29]. It is therefore of pivotal importance to study both the intrinsic parameters of the catalysts and the structure of the catalyst/electrolyte interface.

2.4.1 Hydrogen evolution reaction

The HER reaction mechanism consists of two steps. The first step is always the hydrogen adsorption on the catalyst surface (Volmer reaction):

$$\text{H}^+ + \text{e}^- \rightarrow \text{H}^*$$  \hspace{1cm} (Equation 3)

The second step can be either the reaction of the adsorbed hydrogen with a proton from the electrolyte (Heyrovsky reaction):

$$\text{H}^+ + \text{H}^* + \text{e}^- \rightarrow \text{H}_2$$  \hspace{1cm} (Equation 4)

Or the reaction between two adsorbed hydrogens (Tafel reaction):

$$\text{H}^* + \text{H}^* \rightarrow \text{H}_2$$  \hspace{1cm} (Equation 5)
In either reaction mechanism described, i.e. Volmer-Heyrovsky or Volmer-Tafel, the HER includes only hydrogen as adsorbed intermediate. The first adsorption step, i.e. the Volmer reaction, is thus considered as the rate limiting step and the catalytic descriptor of the HER kinetic.

For the HER the volcano relationship is formed via the plot of the experimentally measured exchange current density \(j_0\) vs. the calculated free energy of hydrogen adsorption \(\Delta G_{H^+}\) described by the Volmer reaction (see Figure 3).

![Figure 3: Experimentally measured exchange current \(j_0\) for HER over different metal surfaces plotted as a function of the calculated hydrogen chemisorption energy per atom \(\Delta G_{H^+}\). Adapted from reference [30].](image)

The most active metal for the HER is Pt, which is the state-of-the-art catalyst for the water-splitting technology at the cathode side.

### 2.4.2 Oxygen evolution reaction

In the case of the OER several reaction mechanisms have been proposed [29, 31, 32]. For metal oxides the most common proposed reaction mechanism consists of four consecutive coupled proton and electron transfer steps:

\[
\begin{align*}
\text{H}_2\text{O} + * & \rightleftharpoons \text{OH}^* + \text{H}^+ + e^- & (\text{Equation } 6\text{A}) \\
\text{OH}^* & \rightleftharpoons \text{O}^* + \text{H}^+ + e^- & (\text{Equation } 6\text{B}) \\
\text{O}^* + \text{H}_2\text{O} & \rightleftharpoons \text{OOH}^* + \text{H}^+ + e^- & (\text{Equation } 6\text{C}) \\
\text{OOH}^* & \rightleftharpoons * + \text{O}_2 + \text{H}^+ + e^- & (\text{Equation } 6\text{D})
\end{align*}
\]
When the surface binds the oxygen too strongly, the reaction is hampered by the OOH* species, while when the oxygen binds too weakly, the OH* oxidation limits the kinetics. Given the fact that the calculated energy difference between OOH* and OH* is constant, the descriptor currently used for the OER activity is the free energy difference between $\Delta G_{\text{OH}^*}$ and $\Delta G_{\text{O}^*}$ (see Figure 4).

![Figure 4: Volcano plot for OER from ref. [33]. The negative values of theoretical overpotential are plotted against the standard free energy of $\Delta G_{\text{O}^*}$ and $\Delta G_{\text{OH}^*}$ step.](image)

For the OER the catalysts showing the highest activity are RuO$_2$ and Co$_3$O$_4$, which are among the current state-of-the-art catalysts in acidic and alkaline solution, respectively [34].

### 2.4.3 Chlorine evolution reaction

The kinetics of CER are still under debate. The main difficulties arise in the determination of the reaction intermediates. In fact, it is still not possible using modern spectroscopic techniques to identify the chemical nature of the adsorbate intermediates in aqueous solutions. The two pathways which are considered the most probable are the following:

\[
\text{Cl}^- \rightleftharpoons \text{Cl}^* + e^- \quad \text{(Equation 7A)}
\]

\[
\text{Cl}^* + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{H}^+ + e^- \quad \text{(Equation 7B)}
\]

\[
\text{HClO}^* + \text{H}^+ + \text{Cl}^- \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O} \quad \text{(Equation 7C)}
\]

And the second:

\[
\text{H}_2\text{O} \rightleftharpoons \text{OH}^* + \text{H}^+ + e^- \quad \text{(Equation 8A)}
\]

\[
\text{Cl}^- + \text{OH}^* \rightleftharpoons \text{HClO} + e^- \quad \text{(Equation 8B)}
\]

\[
\text{HClO} + \text{H}^+ + \text{Cl}^- \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O} \quad \text{(Equation 8C)}
\]
The two proposed mechanisms differ by the first adsorbed reaction intermediate, i.e. Cl* for the first reaction mechanism, and OH* for the second reaction mechanism.

Trasatti described the relationship between OER and CER for oxide catalysts, comparing the activity of different materials at the same current density [35]. He demonstrated that the catalytic activities towards OER and CER are linearly correlated and their linear correlation had a slope close to 1. In fact, the two reactions are reported to compete for the same reaction sites at the catalyst [36], and their reaction energies may be described by the same energy descriptors as can be seen in the volcano plot in Figure 5.

Figure 5: Comparison of Sabatier volcanoes for OER (blue dotted) and CER (black dotted) from Hansen et al. [36]. Potential energies are plotted against the adsorption energies of intermediates on various (110) rutile oxide surfaces. Different reaction pathways involving ClO*, Cl(O*)_2 and Cl* intermediates (from left to right) are plotted. The domain of the most stable surface structure as a function of potential and oxygen binding energy is marked by grey lines. The solid black line shows the combined Sabatier volcano taking into account the stability of the active sites for a given mechanism.

The OER and the CER have similar standard potentials (1.23 and 1.36 V, respectively) at room temperature and normal conditions. The OER is thermodynamically favored but being a 4e⁻ transfer reaction, it is kinetically hindered as compared to the CER [37]. The two gases are thus evolved simultaneously. In industrial chlorine production, the OER is a parasitic reaction and its ratio to the CER decreases with increasing current density.
2.5 Problem identification in electrocatalysis

The main function of catalysis is the reduction of the energy consumption of a chemical process. Therefore, a catalyst is a compound whose function is the decrease of the activation energy for a specific reaction without being consumed by it. The part of catalysis dealing with chemical reactions where the reactants and the catalyst have different state of aggregation is called heterogeneous catalysis. Heterogeneous catalysis can in turn divided in different branches with electrocatalysis being one of them. In electrocatalysis the role of the catalysts is to assist the reaction transferring electrons from an electrode to a reactant, or from the reactant to the electrode, thus fostering the chemical formation of the desired products. Among industrially relevant electrocatalytic reactions, electrochemical production of gases occupies a fundamental role. As examples of these reactions one can mention the production of important reagents such as Cl₂ [17], F₂ [38], H₂ [39], and O₂ [40]. These electrocatalytic reactions involve chemisorption of reactants and reaction intermediates at an electrode surface. The efficiency of the reaction is determined by the ability of the electrode to catalyze the conversion between these reaction intermediates and the products. The conversion rate is determined by the properties of the interface formed at the electrodes in contact with the aqueous or gaseous media. Consequently, in order to rationally develop new generations of electrocatalytic materials or optimize existing systems, it is essential to understand electrified interfaces, predict their properties, and, most importantly, be able to design them purposefully.

Knowledge of the interface and of the gradient of potential in the electrochemical double layer can lead to the control of the reactions occurring in this region, such as the adsorption of reaction intermediates. In fact, ionic and molecular adsorption as well as dipole orientation depend on the sign and magnitude of the charge separation at the interphase. Electrocatalytic reactions always proceed through adsorption steps that are either directly sensitive to the charge or indirectly sensitive through the competition with other adsorbed species or even adsorbed water. The best electrocatalyst is that material which provides a compromise between the activation of reactants and poisoning of the surface with reaction intermediates.

According to the current understanding, at a given electrode potential the properties of the electrochemical interface are essentially determined by the nature of the electrode material [41], its surface structure [42], and the electrolyte composition [43–45]. Fundamental understanding of these determining factors affecting the electrochemical interface leads to comprehension of electrocatalytic reactions.
For electrochemical reactions taking place in aqueous solution, understanding the role of H$_2$O is fundamental. In fact, even H$_2$O can lower the reaction energy barriers acting as an intermediate and permit reactions pathways via auto-protolysis, or act as inhibitor blocking interface sites necessary for the reaction [46–49].

In a wider context, the role of H$_2$O in electrochemical science has been the subject of numerous studies since Lange and Miscenko (1930$^{th}$) [50], who introduced the idea that solvation affects the “equilibrium” potentials at the metal/electrolyte solutions. Owing to this idea several models for the quantification of the water dipole influence have been developed, focusing on the solvent entropy-electrode charge relation in terms of an oriented water layer at the interface [51–54]. On the other hand, difficulties in instrumental probing of the electrified interface hamper the experimental calculation of the aforementioned relation. This is largely due to difficulties in decoupling the response of the bulk water from the response of the water interacting at the interface. Thus, the main contribution to the understanding of water-interface interaction comes nowadays from experiments performed under ultra-high vacuum conditions or/and quantum chemistry calculations.

One of the feasible experimental methods to study the electrode/electrolyte interactions selectively at the interface is the laser-induced potential transient (LIPT) method [55–57]. This technique is based on a sudden increase of the temperature at the electrode/electrolyte interface and permits investigations of the orientation of interfacial water in-situ. The response of the electrode potential to the change of temperature under coulostatic conditions reflects the change in polarization of water molecules. The potential of turnover of the interfacial water network (i.e. when the change of the preferential orientation towards the metal occurs) is defined as potential of maximum entropy (PME) of the double layer formation. The PME is one of the most important parameters in electrochemical surface science, being the potential at which the electrified solid/liquid interface changes its basic properties.

Due to the fact that water dipoles interact electrostatically with the electric field at the interface, the PME is related to the potential of zero charge (E$_{PZC}$). For instance, when the electrode surface is “negatively charged”, the water molecules and electrolyte components are effectively oriented at the surface with the positive dipole toward the electrode.

The concept of E$_{PZC}$ was introduced by Frumkin [58] and it is a fundamental property of the metal/electrolyte system, being defined as the potential at which there is no net-surface charge
at the interphase. The $E_{PZC}$ of transition metals is closely related to their work function $\phi^M$ and their relation can be written as:

$$E_{PZC} = \phi^M e + K$$

(Equation 9)

Where $K$ represents the potential influence of the solvent to the $E_{PZC}$ of the electrode. The work function is defined as the minimum energy required to extract an electron from the Fermi level of a solid carrying no net charge [59], therefore it is one of the key parameters in understanding the interfacial properties of a catalyst. In the early 70s´ Trasatti demonstrated that the work function of a transition metal can be used to describe its activity towards an electrocatalytic reaction, linearly correlating their measured $\phi^M$ to their activities towards HER [60]. An investigation over the PME and the $E_{PZC}$ could therefore provide useful insights into the electrode/solution interaction and give mechanistic insights into electrocatalytic processes at the interface.

In this work, the PME and the $E_{PZC}$ of Ir(111) as model system are investigated. Ir is an interesting material for electrocatalysis being similar in many chemical and physical properties to Pt. For instance, metallic Ir has been found to be highly active for the hydrogen oxidation reaction (HOR) in alkaline electrolytes [61], and a suitable catalyst for formic acid oxidation [62]. Inversely, its higher (compared to Pt) oxophilicity has been generally proven to be a determining factor on the suppression of the ethanol oxidation reaction and ORR in alkaline solution [63], where OH$_{ad}$ acts as intermediate. Furthermore, Ir is the most resistant to corrosion among the platinum group metals [64, 65]. Ir basic electrochemical properties are much less investigated and consequently less understood compared to Pt, and a study on the PME and the $E_{PZC}$ of Ir(111) can help correlating the electrocatalytic properties of the Pt group metals.

The electrode material, its chemical composition and its surface structure are considered to be of primary importance for electrocatalytic processes, but the electrolyte composition also plays a key role. In case of electrocatalytic reactions, the resulting electrode activity appeared to be also dependent on the electrolyte composition [43–45, 66–69]. Electrolyte composition contributes frequently in a non-trivial manner to the performance of electrocatalysts. Therefore, without multi-parametric experimental probing, it might be extremely difficult to have a comprehensive picture of electrocatalysts and of the processes taking place at the electrode/solvent interface [70, 71].

Recent noticeable breakthroughs in fundamental understanding of the electrode/electrolyte interface have been particularly accomplished via studies of single crystal
surfaces. The main reason is that single crystal surfaces permit the perfect control over the surface structure and simplify the interpretation of experimental data. In fact, for electrocatalysts a number of serious difficulties arise when trying to investigate their properties, especially under industrial reaction conditions. When studying electrocatalytic reactions in an electrochemical reactor, a series of phenomena decrease the energy efficiency. The increase in the driving energy needed to perform the reaction with respect to the reaction theoretical energy calculated based on thermodynamic assumptions is called reaction overpotential. The evaluation of the causes and magnitude of this “extra” energy required to perform the reaction is the first step when performing an experiment. This is a non-trivial problem and entails several challenges which will be presented hereafter. Therefore, the identification and optimization of electrocatalysts require very careful and accurate evaluation of the multiple factors affecting the measured activity.

The acquired knowledge can be used to increase the efficiency of electrochemical reactions taking place in energy conversion and storage devices.

3. Aim of the study

The main goal of electrocatalysis is to relate the rate of electrocatalytic reactions to specific properties of the materials. When these relations are adequately described, it would be possible to formulate the predictive basis for the design and the optimization of catalysts. This predictive basis can only be formulated with a detailed knowledge of the mechanism of the reactions. Despite the numerous breakthroughs in analytical techniques and computational models, the description of the kinetic mechanisms for many electrocatalytic reactions is still unsatisfactory. When the correlation between observed experimental catalytic properties and an electrocatalytic reaction is not understood, electrocatalysis advances rely purely on experimental trials. In order to avoid this way of proceeding, factors affecting the electrocatalytic properties of materials have to be identified and the ones governing the catalytic activities need to be isolated.

Computational science has accomplished many achievements over the past years, but it has not reliably mastered the calculation of the interactions between electrified interfaces and aqueous solutions. Therefore, there is still a lack of tools for the computational screening of possible new electrocatalysts and a detailed understanding of the electrocatalytic reactions in aqueous solutions. Electrocatalytic experiments performed on model systems, as single crystal electrodes, can bridge the gap between computational and experimental investigation. In fact, the
use of defined crystallographic planes provides a defined surface structure, reducing the variables of the system under investigation and the computational effort. In order to bridge the gap, in the present work the determination of fundamental properties as the PME and E_{PZC} has been performed on a Ir(111) single crystal surface.

In case of single crystal electrochemistry, an extensive characterization of the catalyst surface can be obtained by the use of defined voltammetric fingerprints, which are extremely sensitive to structure changes. On the other hand, the interface of polycrystalline materials is described by averaging the results of a local surface characterization over the whole surface. The electroactive surface area can therefore differ significantly from the experimentally determined surface area, leading to misleading assessments of the catalytic properties. In fact, the electrocatalytic activity, especially for gas evolution reactions, is governed by reaction sites where the formation and release of bubbles are more rapid. Furthermore, a relative error in the determination of the surface area leads in turn to an incorrect normalization of the measured current. The absence of a standardized procedure for the characterization and evaluation of the catalysts introduces a fluctuating error in the experimental activities reported in literature. To overcome this issues, a new benchmarking procedure for oxide based electrocatalysts is proposed hereafter.

Another critical aspect in the field of electrocatalysis is the lack of understanding of the influence of electrolyte components on the measured activities. Just in recent times the influence of so-called spectator ions was brought into consideration and their influence on electrocatalytic reactions revealed to be bigger than expected. In the present work, the effect of spectator ions on electrocatalytic reaction as HER and OER is investigated by using model single crystal surfaces.

In short, the scope of the present work is the derivation of the intensive properties of electrocatalysts, so as to provide new insights into electrocatalytic reactions and rationalize the investigation of new materials. It is in fact necessary to find a common ground in the field of electrocatalysis, where data obtained by different working groups can be compared and the factors governing the electrocatalytic activities of the different materials can be isolated.
4. Theoretical background

4.1 Reaction overpotential

An electrochemical reaction is composed of different reaction steps, each requiring an activation potential. The potential to drive the reaction determines in turn the value of the current density. The different reaction steps thus govern the electrochemical reaction rate $\nu$, which is directly proportional to the current density $j$:

$$\nu = \frac{j}{nF}$$  \hspace{1cm} (Equation 10)

where $n$ is the number of moles of reactants, and $F$ is the Faraday constant. The current density measured ($j_{\text{meas}}$) is dependent on both the current associated with the activation overpotential ($j_{\text{act}}$) and the current associated with the mass-transfer overpotential ($j_{\text{ms}}$), as described in Equation 11:

$$\frac{1}{j_{\text{meas}}} = \frac{1}{j_{\text{act}}} + \frac{1}{j_{\text{ms}}}$$  \hspace{1cm} (Equation 11)

The presence of a mass transport overpotential leads to a deviation from the exponential dependence of the current with respect to the potential. Ideally the contribution of either $j_{\text{act}}$ or $j_{\text{ms}}$ to the total current needs to be quantified, in order to study the kinetics of an electrode reaction. The mass transport overpotential can be determined by the control of the diffusion of reactants and products. The mass transport current can be expressed as:

$$j_{\text{ms}} = \frac{nFD(C - C_s)}{\delta}$$  \hspace{1cm} (Equation 12)

Where $D$ is the diffusion coefficient and $\delta$ is the diffuse layer thickness, $C$ is the concentration of the reactant in the bulk, and $C_s$ is the concentration of the reactant at the surface.

When $C_s = 0$, the reaction is under diffusion control and the hydrodynamic equations for the system can be solved. Thus, the influence of the mass transport on the overpotential can be quantified and $j_{\text{meas}}$ coincides with the diffusion limited current density $j_{\text{limited}}$.

The mass transport plays a fundamental role especially in gas evolution reactions, where the continuous removal of the evolved gas is necessary in order to avoid blockage of the surface. The mass transport consists of three processes:

- diffusion, defined as the movement of species across a concentration gradient
• convection, defined as the movement of species due to perturbation of the electrolyte caused by pressure gradient
• migration, defined as the movement of species induced by a potential gradient

When forced convection is applied to the solution, the rate of mass transport at the electrode is increased considerably with respect to a system having the sole effect of diffusion processes. This is an effective method to diminish the relative contribution of the reaction overpotential caused by mass transport. The forced convection permits furthermore the measurement under steady state condition, i.e. when the charging of the double layer does not play a role in the measurement. The most common method to obtain a forced convection is the use of a rotating disk electrode (RDE).

4.2 Rotating Disk Electrode

A typical RDE set-up consists of a disk shaped electrode modified with the desired catalyst mounted on a rotating shaft. The electrode is then rotated around its axis perpendicular to the surface of the disk being in contact with the solution. The rotation forces the flow of the electrolyte along a defined pattern, increasing the removal rate of the reaction products and the feeding rate of the reactants towards the surface. With the use of the RDE method the diffusion limited current density $j_{\text{limited}}$ can be calculated as:

$$j_{\text{limited}} = 0.62nFD^2\omega^{1/2}v^{-1/6}C$$  
(Equation 13)

where $\nu$ is the kinematic viscosity of the electrolyte, $C$ is the concentration of the reactant in the bulk, $D$ the diffusion coefficient, $n$ is the number of electrons transferred in the reactions, and $\omega$ is the rotation rate. For gas evolution reactions such as OER and HER it is not possible to reach the regime in which $j_{\text{limited}}$ could be measured. Nonetheless, the use of the forced convection method enables a faster removal of the gaseous products, reducing the relative contribution of the mass transfer overpotential to the reaction kinetics.

When the rate of a reaction is limited by a combination of mass transport and sluggish kinetics, it is often possible to use a rotating disk electrode to elucidate both the mass transport parameters (such as the diffusion coefficient) and the kinetic parameters. These systems can be described by the Koutecky-Levich equation:

$$\frac{1}{j_{\text{meas}}} = \frac{1}{j_{\text{act}}} + \frac{1}{\omega^{1/2}v^{1/6}} \frac{1}{0.62nFD^2C}$$  
(Equation 14)
The plot of $1/j_{\text{meas}}$ against $(\omega^{-1/2})$ yields a straight line with an intercept equal to the reciprocal kinetic current ($1/j_{\text{act}}$). With RDE experiments performed at different $\omega$ and using the Koutecky-Levich analysis it is therefore possible to gain mechanistic insights into the reaction.

### 4.3 Ultra-micro electrode

The second method to increase the mass transport at the surface is the use of ultra-micro electrodes (UME). UME is defined as an electrode which shows hemispherical diffusion in the timescale of the performed experiment [72]. UMEs typically have a critical dimension lower than 25 $\mu$m [73]. The mass transport is enhanced because the diffusion layer thickness is large if compared with the critical dimension, so the current steady-state conditions are fulfilled when the diffusion field grows to a thickness of 100 $\mu$m, for a disk electrode having $d=25$ $\mu$m.

Equation 15 describes the steady state current ($j_{ss}$) at the surface of a disk UME:

$$j_{ss} = 4nFDCr_0$$  \hspace{1cm} (Equation 15)

where $r_0$ is the radius of the UME, and $n$ is the number of electrons transferred. In the case of a disk UME the increase in mass transport at the electrode is defined by the hemispherical diffusion regime. The mass transport to the electrode of a UME is therefore high, even in the absence of convection. The hemispherical diffusion profile at an UME allows faster mass transport of the reactant towards the edges of the electrodes leading to a non-uniform current density profile at the disk UME.

### 4.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy has been used since the 1970s to determine the uncompensated resistance in an electrochemical cell [74–76]. Nowadays, electrochemical impedance spectroscopy (EIS) is an established routine method for the analysis of processes at the interface and resistances of electrochemical reactors. The distinctive feature of this technique is its ability of decoupling the response of the system to the probing signal into different components. The different components of the response describe important processes occurring at the interface such as adsorption and faradaic processes and the uncompensated resistance of the system [77].

EIS is based on probing the electrochemical system with a sinusoidal AC potential perturbation and recording of the output current generated by the response of the system. The probing signal is a sinusoidal wave with an amplitude small enough to generate only a linear response of the system. The response is a sinusoidal current signal with the same frequency but a
phase shift with respect to the probing signal. The impedance of the system represents the
transfer function of the system to a potential (or current) perturbation and it can be defined as:

\[ Z(\omega) = \frac{F[E_0 \sin(\omega t)]}{F[I_0 \sin(\omega t + \phi)]} \]  
(Equation 16)

Where \( Z(\omega) \) is the impedance of the system, \( F \) represents the Fourier transform at the angular
frequency \( \omega \), \( E_0 \) is the amplitude of the potential oscillation, \( I_0 \) is the amplitude of the current
oscillation, \( \omega \) is the angular frequency where the frequency \( f = 2\pi\omega \), \( t \) is the time, and \( \phi \) is the
phaseshift. The impedance represents a generalization of Ohms’s law to non stationary pertur-
bations. In Equation 16 the denominator is the current response to the probing signal, with a
phase shift determined by the properties of the electrochemical system. Using the Euler’s
relationship the impedance can be represented as a complex function:

\[ Z(\omega) = Z_0 e^{i\phi} = Z_0 (\cos \phi + i \sin \phi) \]  
(Equation 17)

The impedance complex function thus consists of an imaginary and real part. When the real part
of the impedance is plotted as the x-axis and the imaginary part as the y-axis, a “Nyquist plot” is
created. Another common method of representation of the impedance is the “Bode plot”, in
which the \( \log(f) \) (x-axis) is plotted against the absolute values of the impedance and the phase
shift (both as y axis).

4.5 Potential of maximum entropy and laser induced potential transient
method

The aim of the laser-transient technique is the in situ investigation of the
electrode/solution interface. A schematic representation of the apparatus used for the laser
induced potential transient (LIPT) experiments is depicted in Figure 6.
LIPT is used to investigate the kinetic and thermodynamic phenomena which produce a change in the open-circuit potential in response to a change in the interfacial temperature. Nanosecond laser pulses are fired to the interface to instantaneously increase the temperature at the electrode-solution interface while the potential response of the interface toward the laser heating is measured under coulostatic conditions. The perturbation caused by the laser destroys the equilibrium between the double layer potential and redox potential, causing a potential shift. The shift in the potential reflects the system’s attempt to re-establish equilibrium under the new conditions. The potential shift responds to phenomena that occur in the nanosecond time range such as the reorientation of water dipoles towards the surface.

The energy density of the applied laser beam is low enough to avoid damage or photo-emission of electrons from the electrode, e.g. the $\Phi^M_{\text{Pt(111)}} = 5.4 \text{ eV}$, a value higher than the energy of the laser photons [56]. Therefore, the laser pulse only affects the temperature of the interface and probes the double layer selectively. The change in the temperature cannot be directly measured due its short time scale (i.e. ns) but it can be estimated by applying a thermal transfer model. The thermal model considers that the non-reflected portion of the energy is immediately converted into heat [55]:

$$\frac{\partial^2 \Delta T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial \Delta T}{\partial t}$$  \hspace{1cm} (Equation 18)
where $\alpha$ is the thermal diffusivity of the solution and $\Delta T$ is the change in temperature caused by the laser. Solving the partial differentiation by applying the corresponding boundary conditions, it is found that for long decay times after the laser pulse ($t >> t_0$), the maximum temperature change $\Delta T$ corresponds to:

$$\Delta T = \frac{1}{2} \Delta T_0 \sqrt{\frac{t_0}{t}}$$  \hspace{1cm} \text{(Equation 19)}$$

The response of the interface to the thermal perturbation under coulostatic conditions is a potential drop across the double layer that follows the change in the temperature. When the change of the temperature is sufficiently small, i.e. at $t >> t_0$, the reorganization of the interface is faster than the time scale of the temperature perturbation. The change of the potential in this case is described by:

$$\Delta E = \left( \frac{\partial E}{\partial T} \right)_q \Delta T = \frac{1}{2} \left( \frac{\partial E}{\partial T} \right)_q \Delta T \sqrt{\frac{t_0}{t}}$$  \hspace{1cm} \text{(Equation 20)}$$

Where the term $\left( \frac{\partial E}{\partial T} \right)_q$ is the thermal coefficient of the double layer. Hence, if the reorganization of the double layer is fast enough with respect to the employed time scale and the change in temperature is small, then the thermal coefficient that can be extracted from the slope of $\Delta E$ vs $1/\sqrt{t}$ (see Figure 7).

Figure 7: (A) potential change at $t >> t_0$ caused by the double layer reorganization vs. $1/\sqrt{t}$. (B) slopes of the potential transient vs the potential of the electrode. LIPT experiment performed on Ir(111) in 0.01 M HClO$_4$ + 0.99 M KClO$_4$ electrolyte (pH 2).
The plot of the electrode potential response to the change in temperature thus gives a measure of the temperature coefficient of the double layer potential. In absence of specific adsorption phenomena, this coefficient is related to the entropy of formation of the double layer:

\[
\frac{\partial E}{\partial T}^M = -\left( \frac{\partial \Delta S_{dl}}{\partial q} \right)_T
\]

(Equation 21)

Where \(\Delta S_{dl}\) is the entropy of the double layer and \(q\) is the double layer charge.

The potential at which the temperature coefficient of the double layer potential becomes zero corresponds to the potential of maximum entropy of formation of the double layer. If the solution contributes positively to the potential of the electrode, the laser pulse provides a negative E-t transient. On the other hand, at more positive potentials, the dipolar contribution of the solution is negative and the laser potential transient obtained is positive. At the applied potential at which there is no net dipolar contribution, the intensity of the obtained laser transient is zero. This potential corresponds to the PME and is closely related to the potential of zero charge.

When calculating the potential drop due to the thermal perturbation, the potential drop caused by the temperature difference between the reference and the working electrode should also be taken into account. This potential drop is called thermodiffusion potential and it can be estimated by knowing the Eastman entropies of transport of the different ions in the electrolyte:

\[
\frac{\partial E_{thermodiffusion}}{\partial T} = -\frac{1}{F} \sum \frac{t_i}{z_i} S_i
\]

(Equation 22)

Where \(t_i\), \(z_i\) and \(S_i\) are the transport number, the charge and the Eastman entropy of transport of the ion \(i\), respectively.

4.6 Point of Zero Charge and CO-displacement method

Among the properties characterizing the structure at the interface, the importance of the E_PZC has often been stressed [79–81]. In fact, as mentioned in chapter 2.5, one of the key parameters in understanding the interfacial properties is the work function of a metal, which is closely related to the E_PZC [60, 82]. Furthermore, the pH dependence of the E_PZC reveals key aspects of the solvent structure at the interface [83, 84].

The concept of the E_PZC was introduced by Frumkin in the late 1920s [58] and has been recognized as a key requirement for the understanding of double-layer properties ever since. E_PZC was first measured on a liquid mercury electrode, where its value can be easily extracted from electrocapillary curves [85]. On the other hand, the measurement of E_PZC on solid electrodes was
delayed by the existence of intrinsic experimental difficulties. Surface heterogeneities complicated the interpretation of the obtained result and the accumulation of impurities on the surface may strongly affect the double layer structure. Ultrapure solutions and the development of suitable methods for electrode cleaning without affecting its surface atomic structure greatly improved the accuracy. Studies of the electrochemical behavior of individual single crystals were of pivotal importance for the development of $E_{PZC}$ measurements, especially after the development of the so-called “flame-annealing technique” by Claviller et al. [86], which enabled the production of high-quality single crystal surfaces for platinum group metals. In absence of specific adsorption, the most common method for the evaluation of $E_{PZC}$ is the measurement of the differential capacitance of the double layer as a function of the potential in dilute solutions. The minimum of the differential capacitance corresponds to the $E_{PZC}$, as predicted by the Gouy-Chapman theory.

For metals in aqueous solutions, where electro sorption of hydrogen and hydroxyl/o xide species occurs, $E_{PZC}$ determination is less straightforward. Voltammetry cannot distinguish between oxidative adsorption of an anion or oxidative desorption of a cation because it is a technique which is not sensitive to the chemical nature of the adsorbed species. When hydrogen and hydroxyl adsorption occur in the same potential range, it is not possible to distinguish the two processes from simple voltammetric measurements. This is the case for Platinum group metals that adsorb hydrogen and hydroxyl at the surface. Platinum group metals like platinum, palladium, rhodium, and iridium are indeed some of the most electrocatalytically active materials for HER and HOR.

When hydrogen and hydroxyl ions adsorb at the interface, the potential of zero total charge ($E_{PZTC}$) has to be defined, where the charge involved in the adsorption is included. For Platinum group metals the $E_{PZTC}$ values have been summarized by Petrii [81]. When no adsorption process occurs at the interface, $E_{PZC}$ is redefined as point of zero free charge ($E_{PZFC}$). At $E_{PZFC}$, the charge measured is the catalyst’s “true electronic charge”, without involvement of adsorption processes. Only the $E_{PZTC}$ (which coincides with the $E_{PZFC}$ in the absence of specific adsorption) is experimentally accessible. Nevertheless, $E_{PZFC}$ can be derived from $E_{PZTC}$ under a series of assumptions for catalysts whose $E_{PZC}$ of the CO covered surface has been inferred from UHV measurements [87].

The development of the so-called “CO-displacement method” by Feliu et al. has been a notable breakthrough in the $E_{PZC}$ determination for these catalysts [88–90]. This method uses an
inert chemisorbed model species, namely CO, to “displace” the double layer. The potential-dependent charge measured upon “displacing” the double layer is then used to quantify the surface charge. At a given electrode potential, the change in surface charge is induced by removal and formation of the aqueous double layer by CO. \( E = E_{\text{PZTC}} \) is then defined as the potential at which the surface charge of the metal equals 0. The main advantage of this technique consists in its ability to rapidly suppress the surface charge at a given electrode potential by CO adsorption, thereby evaluating it by purely in-situ means.

The CO-displacement technique consists of a few simple steps. At first, prior to each CO-displacement, voltammetric profiles are recorded to assess the status of the crystal. Secondly, the electrode potential is fixed and CO is flushed through the solution. CO is adsorbed at the interface and a transient in the amperometric profile corresponding to the displaced charge is recorded. Upon integration of the current transient, the charge at the interface is determined. After that, CO is removed from the solution in an inert gas flow (usually Ar) and the surface is finally recovered to its initial state via CO stripping.
5. Results and discussion

5.1 Uncompensated resistance correction

Ohmic losses of a given system, together with the kinetics, mass transport and thermodynamics of the reaction constitute the three fundamental components of the energy consumption of the system. The uncompensated resistance, even though it is not the main focus of the electrochemical investigation, plays an important role in the determination of the overvoltage needed for a certain reaction. The uncompensated resistance inside an electrochemical cell is the sum of all ohmic losses that the current encounter between the working electrode connection of the instrument and the reference electrode. Their sources are of various nature but can be divided into three major groups [91]:

- Electronic resistivity of the working electrode
- Resistivity within the electrical circuit and cables of the electrochemical instrumentation
- Resistances due to ionic migration within the electrolyte

The resistance of the electrical circuit and of the working electrode are usually of minor relevance. The uncompensated resistance is assumed to be equal to the resistance of the electrolyte between the working and the reference electrodes. The solution resistance is influenced by several parameters such as temperature, solution conductivity, and geometrical arrangement of the cell which influences the current distribution. Once temperature and solution are fixed, the solution resistance is entirely dependent on the distance between working and reference electrode and on the current distribution inside the electrochemical cell.

There are several parameters complicating the evaluation of the uncompensated resistance using EIS and they require particular attention and additional procedures which are normally ignored. When performing EIS, the impedance related to the uncompensated resistance is extracted at high frequencies, where it is related to bulk ionic and electronic resistance as well as contact resistances. In a Nyquist plot the uncompensated resistance can then be easily visualized by the intersection of the impedance spectra with the real number axis [92].

Nevertheless, the ideal approach to determine the uncompensated resistance is by fitting the experimental spectra with an equivalent electrical circuit (EEC). The components of the EEC can be associated with a physical model describing the processes occurring in the electrochemical system. Modelling EEC to describe the electrode/electrolyte interface is a convenient approach to
extract information from the impedance spectra. In fact, by fitting the experimental curve with
the appropriate EEC, the values corresponding to the double-layer capacitance, charge-transfer
resistance, and uncompensated resistance can be extracted. Figure 8A represents the impedance
spectra for two simulated system with and without faradaic process occurring at the interface. In
both cases the EEC is adapted accordingly. When a faradaic reaction occurs, a resistance in
parallel to the double layer capacitance is inserted in the EEC, in the most straightforward case.
This resistance represents the charge-transfer resistance of the faradaic process at the interface.
This procedure can turn out to be more complicated when fitting non simulated data. As an
example in Figure 8B an impedance spectrum recorded using a dummy cell is presented.

Figure 8: EIS spectra represented as Nyquist plots. (A): Simulated spectra for two separate cases
with (◇) and without (○) faradaic processes. R_U is the uncompensated resistance, C_DL is the capaci-
tance of the double layer, and R_CT is the charge transfer resistance. The high-frequency parts of
both spectra intersect the real-number axis at the value of the uncompensated resistance (in this
case 50 Ω). (B): EIS spectra taken with a dummy cell with the circuit shown in the inset, without
(×) and with (●) a shunt capacitance connected. Frequencies: 1 MHz – 100Hz. Values of the
equivalent electric circuit elements: R_1 = 100 Ω, R_2 = 1kΩ, and C_1 = 2 µF. From ref. [93].

In Figure 8B the high-frequency region of the spectrum shows two semicircles instead of
one. The high-frequency part of the spectrum becomes distorted and does not intersect the real
axis. In this part of the spectrum, the value of the imaginary part of the impedance rises thus
leading to a second semicircle. This can be considered as an artefact due to the limitations of the
potentiostat amplifiers or stray capacitances. At high frequency the sine waves are filtered out by
the RC circuit formed by the stray capacitance of the reference circuit with the resistance of the
One easy method to overcome the limitation of the control amplifiers is to insert a shunt capacitance between the reference and the counter electrode. The shunt capacitance, commonly named capacitor bridge, eliminate the non-ideal behaviour of the system at high frequencies, permitting the high-frequencies to bypass the RC filter formed by the cell [94, 95]. The shunt allows the transmission of high frequencies directly into the solution via the counter electrode, thus bypassing the reference electrode. The capacitance of the shunt is usually set by a trial and error procedure [94]. With the insertion of the capacitor bridge, the spectrum of the impedance intersects the real-number axis and the semicircles formed at high frequencies is eliminated (see red circles in Figure 8B). Figure 9 shows impedance spectra of Pt(111) electrodes taken in a solution containing 0.05 M H\textsubscript{2}SO\textsubscript{4} and 0.05 M Rb\textsubscript{2}SO\textsubscript{4} to provide an example of the effect of the capacitor bridge on an actual electrochemical system.

Without the capacitor bridge the distortion at high frequencies is present in both spectra. In Figure 9 the value of the uncompensated resistance determined without the use of a shunt capacitance has an associated error of \( \sim 20\% \).

![EIS spectra of Pt(111) in Ar-saturated 0.05 M H\textsubscript{2}SO\textsubscript{4} and 0.05 M H\textsubscript{2}SO\textsubscript{4} + 0.05M Rb\textsubscript{2}SO\textsubscript{4}, with (●,■) and without (○,□) the shunt capacitance connected between the RE and CE, at OCP. Frequency range: 30 kHz – 100 Hz. RDE configuration, 1600 rpm. From ref. [93].](image)

One further issue concerning the measuring of the uncompensated resistance is the presence of gases in solution. In Figure 10 the change of \( \sim 20\% \) in the uncompensated resistance between an Ar-saturated and a H\textsubscript{2}-saturated solution can be seen. In this case, the change in resistance is dramatic as a Pt electrode was used. Pt adsorbs hydrogen, changing the status of the surface and shifting the open circuit potential (OCP) of the system. If the EIS is performed at
OCP, the measurement in Ar and H₂ saturated solutions is not performed at the same potential, thus changing the uncompensated resistance.

Figure 10: EIS spectra of Pt(111) in 0.05 M H₂SO₄ saturated with H₂ (○) or Ar (●), at OCP. Both spectra are recorded with a connected shunt capacitance. Frequency range: 30 kHz – 100 Hz. RDE configuration, 1600 rpm. From ref. [93].

The fitting of EIS spectra with an appropriate EEC is important especially when spectra are noisy in the high frequency part. The noise may be due to hardware limitations or other kind of interferences and it is of common recurrence. In Figure 11 an example of a noisy spectrum is illustrated.

Figure 11: EIS spectrum with significant noise in the high-frequency area, which makes the determination of the trivial intersect real-number axis less accurate. Inset shows the EEC used for fitting. Adapted from ref. [93].

The noise in the high frequency region leads to an uncertainty of ~1 Ω in the determination of the intersection. The fitting of the experimental spectrum with an EEC reduces
considerably the error associated with the determination of the resistance, here from ~1 Ω to ~0.2 Ω. At a first glance an error of ~1 Ω may seem negligible, but it can severely affect measurements at high current densities. This is the case of gas evolution reactions, such as OER, CER and OER. For these reactions the comparison between different electrocatalysts is often done at current densities in the order of mA cm$^{-2}$. For instance, for OER benchmarking the comparison between different electrocatalysts is often done at current densities of 10 mA cm$^{-2}$ [32, 34, 96]. In these cases, an uncertainty of 1.1 Ω for a 10 mA catalytic current generates an error in the uncompensated resistance correction of ~11 mV. This error is not acceptable for a correct benchmarking of electrocatalysts.

In Figure 12 a gas evolution reaction on Pt, namely HER, is shown to further explain the significance of the uncompensated resistance (iR drop) correction. A voltammogram of this reaction is depicted in Figure 12A without iR drop correction. The kinetic of HER seems significantly faster in perchloric acid than in sulphuric acid at the same pH value. In Figure 12B the two voltammograms superimpose after iR correction. This result is in agreement with the theoretical prediction that the HOR takes place under diffusion control (dotted line in Figure 12B).

![Figure 12: CVs of HER on Pt in H$_2$-saturated 0.05 M H$_2$SO$_4$ (▬) and 0.1M HClO$_4$ (▬). RDE, 1600 rpm (A) without iR-drop correction (B) with iR-drop correction. The dashed line (▪▪▪▪) represents the theoretical curve derived from the Nernst equation. After the correction for the iR-drop, the voltammograms in the two electrolytes align with each other as well as with the theoretical curve.](image)

The results presented agree with the classical catalytic description of the HER. Interestingly, for the HER the reported currents used for benchmark purposes are significantly
different [97–99]. For the sake of simplicity, Figure 12 shows only the low overpotential part of the HER voltammogram. The uncompensated resistance correction (iR drop) for electrocatalytic gas evolution reaction at high overpotential requires further corrections as a non-conductive gas phase is formed at the interface.

When gas is formed during an electrocatalytic reaction, the solution resistance is significantly affected by the emergence of the bubbles periodically or stochastically leaving the surface. The bubble formation influences the uncompensated solution resistance in two ways:

1. The bubbles reduce the electrochemical active surface area of the electrode. This effect is diminished in a RDE setup or in a flow cell configuration, but never completely eliminated. In fact, the developing gas phase still blocks the active sites on the surface, decreasing the effective electrode surface area, even when removing the bubbles via an increasing of the electrolyte flow or an increasing of the rotation rate.

2. The non-conducting gas phase reduces the bulk conductivity of the electrolyte, according to the Bruggeman equation:

\[
R_b = R_e \left(1 - \varepsilon \right)^{\frac{2}{3}}
\]  

(Equation 23)

where \(R_b\) is the electrolyte resistance in the presence of the non-conducting gas phase, \(R_e\) is the electrolyte resistance without the gas phase, and \(\varepsilon\) is the gas phase fraction.

The iR-drop correction is particularly important in gas evolution reactions and it should be performed with great care and under real experimental conditions. In fact, the error introduced with an inaccurate evaluation of the uncompensated resistance increases with increasing electrolyte resistance due to the gas phase, especially at high reaction rates.

To illustrate the significance of the influence of the gas-phase evolution on the uncompensated resistance, a well-known OER catalyst, namely cobalt-oxide, was used as model system (see Figure 13). For gas evolution reactions, the frequency of bubble formation is dependent on the rate of the reaction, and, thus, on the electrode potential. The faster bubble formation at higher potentials increases the uncompensated resistance.
Figure 13: Electrodeposited CoO\textsubscript{x} thin film in 0.1 M KOH (A) EIS spectra during OER 1.4 – 1.77 V vs. RHE. Inset shows the EEC used for fitting. $R_u$ – uncompensated resistance, $R_{ct}$ – charge transfer resistance, $Z_{dl}$ – double layer impedance. Additionally, the EEC contains a parallel connection of an adsorption resistance, $R_a$, and capacitance, $C_a$, connected in series to $R_{ct}$ to account for the behavior of the reversibly adsorbed reaction intermediates. (B) Estimated uncompensated resistances (○) and the uncertainties (●) were determined as a function of the applied electrode potential. From ref. [93].

In Figure 13 one can see that the value of the uncompensated resistance increases from \(~102\ \Omega\) to \(~130\ \Omega\) when the applied electrode potential changes from 1.4 V to 1.77 V. This can lead to significant errors in activity benchmarking if the iR-drop correction is not correctly performed: The error introduced to the determined activity will be different at different potentials, reaching ca. 30% difference in the example in Figure 13, making the comparison of data for different electrocatalysts very difficult. Furthermore, the Tafel slope corrected for the uncompensated resistance changes significantly, leading to an incorrect evaluation of reaction kinetic parameters.

5.2 Electrolyte influence on reversible processes on single crystal surfaces

In order to gain more information about an electrocatalytic reaction, an experiment should ideally be performed on surfaces whose composition and atomic structure are uniform. This is why the use of single crystals in electrochemistry has gained more importance throughout the last decades.

In fact, many electrochemical reactions have been found to be highly dependent on the surface structure, and more insights into their mechanism can be gained \textit{via} the use of surfaces
having different crystalline orientations. The surface atoms, regularly arranged with different symmetry (distinct coordination number), would interact at different energies with the adsorbates, due to the different type and overlap between the local electronic density of a site (metal orbitals) and the adsorbing species. Therefore, the following experiments performed on single crystal electrodes are potential tools to study in a simplified way the effect of surface structure on a given electrocatalytic reaction. The acquired knowledge can then be transferred to understand the experimental results on polycrystalline materials.

In the following experiments, Pt(111) and Ir(111) are used as model surfaces. For both, it is possible to determine the quality of the surface and cleanliness of the electrolyte by examining positions and shapes of voltammetric peaks.

**5.2.1 Anions influence on Pt(111) and Ir(111) voltammetric profiles**

The electrolyte composition can change the status of the electrode/electrolyte interphase and the voltammetric response of the system dramatically. In Figure 14, voltammetric profiles for Pt(111) recorded in Ar-saturated H$_2$SO$_4$ and HClO$_4$ as electrolytes are shown. These two solutions are the “reference” ones used for single crystal characterization in acidic solution, as they are in many cases close to the conditions relevant for practical applications.

![Figure 14: Characteristic CVs of Pt(111) in 0.05 M H$_2$SO$_4$ (red line) and 0.1 M HClO$_4$ (black dots) Ar-saturated solutions. Scan rate 50 mV/s.](image)

In H$_2$SO$_4$ and HClO$_4$ solutions hydrogen is adsorbed/desorbed from the surface in the potential region from 0.05 V to 0.35 V (so-called H-upd region). Pt(111) is characterized by sharp “butterfly” peaks in both solutions. In HClO$_4$, butterfly peaks between ~0.6 V and ~0.8 V
originate from reversible hydroxide adsorption. On the other hand, in H$_2$SO$_4$ the butterfly peaks between ~0.35 V and ~0.55 V vs RHE are caused by (bi)sulfate adsorption. The adsorption of (bi)sulfate begins after the hydrogen adsorption region and leads to the formation of an ordered $\sqrt{7} \times \sqrt{3}$ structure with a (bi)sulfate coverage of ~0.20 [100]. Changing the anion from ClO$_4^-$ to SO$_4^{2-}$ has one main effect on the voltammetric profile: sulfates compete for the active sites at the platinum surface, hence suppressing OH-adsorption. The latter reveals itself with a pair of small peaks caused by OH adsorption [101] between ~0.7 V and ~0.8 V. In 0.1 M HClO$_4$, a double-layer charging region is present between the H-upd and the reversible hydroxide adsorption regions, i.e. from ~0.35 V to ~0.55 V.

The influence of the anion in acidic supporting electrolytes is also remarkable for the other investigated model surface, i.e. Ir(111). The voltammetric profiles in H$_2$SO$_4$ and HClO$_4$ with pH 1 are depicted in black and red, respectively (Figure 15).

![Voltammogram](image.png)

Figure 15: Voltammetric profile of Ir(111) in 0.1 M H$_2$SO$_4$ (black line) and in 0.1 M HClO$_4$ (red line). Ar-saturated solutions. Scan rate 50 mV/s.

The voltammograms in 0.1 M HClO$_4$ and in 0.1 M H$_2$SO$_4$ are similar to the ones reported previously in literature [102–107], proving the benchmarking quality of the model surface. In HClO$_4$ the voltammetric profile shows characteristic features resembling the one recorded for Pt(111) in 0.1 M HClO$_4$ (see Figure 14); the H-upd at low potentials (from 0.05 V to 0.3 V) is followed by a double-layer charging region, and at more positive potential, i.e. ~0.9 V, a peak suggesting an hydroxide adsorption. The voltammogram in HClO$_4$ is not symmetrical to the potential axis, revealing irreversibility in the reverse scan. Therefore, it can be supposed that
hydrogen and hydroxide adsorption are slower than on Pt(111), as inferred by Kolb et al. [102] from impedance analyses.

According to the current understanding voltammetric profiles of Ir(111) in H$_2$SO$_4$, the peak at ~0.05 V vs RHE is assigned to sulfate adsorption/desorption. During the anodic sweep, sulfate replaces the hydrogen ad-atoms and covers the surface until irreversible oxide formation occurs (~1.35 V vs RHE)[107]. Ito et al.[107] and Itaya et al.[108] confirmed the presence of adsorbed sulfates in 0.1 M H$_2$SO$_4$ electrolyte via infrared adsorption spectroscopy (IRAS) and scanning tunnel microscopy (STM). Results obtained by IRAS identified the vibrational modes characteristic for the adsorption of sulfate ions [107] and STM measurements detected an ordered $\sqrt{7} \times \sqrt{3}$ sulfate structure on the Ir(111) surface [108].

Integration of the area under the sulfate peak results in a charge of 272 µC cm$^{-2}$ in 0.1 M sulfuric acid solution, slightly higher that the theoretical value of 252 µC cm$^{-2}$ corresponding to a hydrogen adlayer with a 1:1 ratio of *H to Ir atoms involving a one-electron-transfer reaction at an ideal Ir(111)-(1x1) surface.

5.2.2 Influence of alkali metal cations on Pt(111) and Ir(111) voltammetric profiles

The influence of alkali metal cations, such as Li$^+$, Na$^+$, K$^+$, Rb$^+$ or Cs$^+$, has then been studied in sulfate-containing electrolytes for Pt(111). Even though they are widely considered as being non-electroactive in aqueous electrolytes, one can observe that these cations contribute to the interface properties. A series of cyclic voltammograms recorded in Ar-saturated 0.05 M H$_2$SO$_4$ + 0.05 M Me$_2$SO$_4$ electrolytes (Me = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) is depicted in Figure 16. The voltammetric profile change significantly with the cation revealing clear trends in adsorption of electrolyte components, similar to findings by Garcia et al. [109]. Alkali metal cations in H$_2$SO$_4$ media influence all the adsorption processes taking place in a given potential region in Figure 16. Their effect is not very pronounced in the case of the hydrogen adsorption and desorption region, while adsorption of (bi)sulfates and *OH are affected more noticeably.
Figure 16: Voltammetric profiles of Pt(111) in (A) 0.05 M H$_2$SO$_4$ and in (B-F) 0.05 M H$_2$SO$_4$ + 0.05 M Me$_2$SO$_4$ (Me = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) electrolytes. Scan rate 50 mV/s. Ar-saturated. From ref. [110].

In Figure 16, CVs only show significant differences in the $^*H$ adsorption/desorption region for the Cs$_2$SO$_4$ containing solution. In this case there is a slight negative shift in the onset of the $^*H$ adsorption/desorption, likely due to adsorption of Cs$^+$ ions similar to the effect reported by Berkes et al. [67]. The pair of sharp peaks at ~0.5 V, which reveals the disorder/order phase transitions in the adsorbed sulfate layers [101], is very sensitive to the nature of the cations and shifts non-linearly (see (bi)sulfate peaks in Figure 17A). The hump denoted in Figure 16 as “$^*$” originates from OH adsorption [100, 111, 112]. STM observations by Braunschweig et al.[101] indicate that the OH co-adsorption provokes the disruption of the $\sqrt{7}$ x $\sqrt{3}$ (bi)sulfate structure on the surface, causing the order/disorder phase transition in the adsorbate layer. For these reasons, we will thereafter refer to the hump denoted as “$^*$” as the order/disorder phase hump. Figure 17 shows that the onset potential for the order/disorder phase hump changes according to the following series Cs$^+ < $Rb$^+ < $K$^+ < Na$^+ < $Li$^+$. This trend is exactly the opposite to that found by
Marković et al. [44] for the *OH adsorption at Pt(111) electrodes in MeOH (Me = Li+, Na+, K+, Cs+) electrolytes.

Figure 17: (A) (●) Dependences of the anodic peak positions for the “(bi)sulfate” adsorption and (O) the order/disorder phase transitions (“*” peak) on the nature of the alkali cations. (B) Integrated anodic parts of the respective voltammograms (corrected for the double layer charging currents) in the range of the potentials between 0.55 V and 0.89 V vs RHE. From ref. [110].

As can be seen in Figure 17, there is a non-linear relation between the (bi)sulfate peaks and the increasing cation radius, as Na+ stabilizes the adsorbed superstructures while Cs+ destabilizes them the most. The potential of the order/disorder hump shifts negatively as the ionic radius of the alkali-metal cations increases. Cations interact with the adsorbed (bi)sulfates having a stabilizing effect by decreasing the repulsion between partially charged species. As can be seen in Figure 18 there is a correlation between the increase in cation hydration energy and the increase of the stabilization of the $\sqrt{7}\times\sqrt{3}$ sulfate adlayer.

Figure 18: Hydration energies vs the potential of the order/disorder hump denoted as “*”. Values of the hydration energies from ref. [113].
A linear correlation is evident in particular for K$^+$, Rb$^+$, and Cs$^+$. In fact, there are large changes in atomic and ionic parameters between Na$^+$ and K$^+$ and comparably small changes between K$^+$, Rb$^+$, and Cs$^+$ [114, 115]. Concerning the physico-chemical properties, the group of alkali metals can be divided into subgroups, with K$^+$, Rb$^+$, and Cs$^+$ belonging to the same subgroup. It is therefore evident from the experimental results, that when the surface is positively charged and anions are adsorbed at the surface, i.e. at $E > E_{PZC}$, alkali metal cations can perturb the adsorbed layer via electrostatic interactions.

The influence of the alkali cation on the other investigated model surface, Ir(111), also becomes evident from the corresponding voltammetric profile in alkaline solution at pH 13 (see Figure 19).

![Figure 19: Voltammetric profiles of Ir(111) in Ar-saturated 0.1 M NaOH (red dots) and 0.1 M LiOH (black line). Scan rate 50 mV/s.](image)

The H-upd region situated between 0.05 V and 0.25 V is followed by a sharp peak caused by OH adsorption, as suggested by CO-displacement measurements performed by Marković et al. [61]. After the OH adsorption peak there is a wide featureless “double layer region” and finally a peak at the anodic end of the potential window. This peak was claimed to represent an additional adsorption of OH$_{ad}$ / O$_{ad}$, yet without experimental findings to prove so [63]. The alkali cation influence on the OH adsorption peak and on the onset of the OH$_{ad}$ / O$_{ad}$ peak is noteworthy. The presence of Li$^+$ increases the gap between the two aforementioned processes initiating the OH$_{ad}$ at lower potentials and shifting the “OH$_{ad}$ / O$_{ad}$ peak” to even higher electrode potentials as compared to Na$^+$. This effect is similar to the one described before for Pt(111) in Figure 14, since
it can be attributed to the cation interaction with the specifically adsorbed anion. In fact, for Ir(111) the cation stabilizes the adsorbate layer via non-covalent interactions between the OH\textsubscript{ad} and the M\textsuperscript{+}(H\textsubscript{2}O\textsubscript{x}) network, where M\textsuperscript{+} represents the alkali cation and (H\textsubscript{2}O\textsubscript{x}) its hydration shell. This is a straightforward example of how an increase in hydration energy (from Li\textsuperscript{+} to Na\textsuperscript{+}) can influence the properties of an adsorbate layer.

5.2.3 Influence of the proton concentration on Ir(111) voltammetric profiles

In the previous paragraphs the influence of the supporting electrolyte at constant acidic pH value of 1 was investigated. However, in the case of hydrogen and OH adsorbing metals such as Ir and Pt, the study of the pH influence on the voltammetric profiles contains valuable information about the structure of the interface. This study, additionally emphasizing on the pH dependence of PME and E\textsubscript{PZTC} can give insights into the state of adsorbed hydrogen and OH species, which are the relevant intermediates for HER, OER, and CER. The effect of the proton concentration in the voltammetric profiles of Pt(111) has been extensively studied [116–118], while this is not the case for the Ir(111) single crystal.

In order to characterize the electrochemical behavior of the Ir(111) single crystal in acidic aqueous electrolytes, cyclic voltammograms of Ir(111) were recorded in HClO\textsubscript{4} solutions at pH 1 and 2 (Figure 20A), and for pH 3, 4, and 5 (Figure 20B).

![Figure 20: Voltammograms of Ir(111) at 50 mV/s: (A) In 0.1 M HClO\textsubscript{4} (pH 1, black), in 0.01 M HClO\textsubscript{4} + 0.099 M KClO\textsubscript{4} (pH 2, red). (B) In 1 mM HClO\textsubscript{4} + 0.1 M KClO\textsubscript{4} (pH 3, black), in 0.08 M KClO\textsubscript{4} + 0.02 M NaF / HClO\textsubscript{4} buffer (pH 4, red), in (0.1 - x) M NaF + x M HClO\textsubscript{4} (pH 5, blue).](image)
The solutions are kept at the same ionic strength by addition of KClO$_4$ for pH 2 and pH 3, and by addition of non-specifically adsorbing NaF for pH 4 and pH 5. NaF has been used as buffer electrolyte at pH 4 and pH 5 to prevent local pH changes near the interface. The region between the cathodic limit of the voltammetric scan and the double-layer region, i.e. the H-upd region, has distinctive features which vary with the pH value. H-upd voltammetric charge is in good agreement with the charge of a hydrogen monolayer on Ir(111), 252 µC cm$^{-2}$ [108], only at pH 1. The charge decreases from 280 µC cm$^{-2}$ at pH 5 to 278 µC cm$^{-2}$ at pH 4, via 260 µC cm$^{-2}$ at pH 2 and pH 3 suggesting the co-adsorption of other ions.

In order to highlight these distinctive features, the voltammetric profiles in the region between 0 and 0.35 V vs RHE are plotted with an enlarged scale (Figure 21). Two peaks at ~0.07 V and at ~0.25 V vs RHE can be clearly distinguished in the CV at pH 1. The first peak is associated with hydrogen oxidation and shifts by ~46 mV from pH 1 to pH 2, ~42 mV from pH 2 to pH 3, and ~38 mV from pH 3 to pH 4. Finally, due to a further shift in potential, the peak associated with hydrogen oxidation at pH 5 is not visible because it merges with the second peak at ~0.25 V vs RHE, the latter being potential-independent on the pH value. Nevertheless, the charge related to the peak at ~0.25 V vs RHE increases steadily as the concentration of protons in solution decreases.

![Figure 21: Details of the anodic sweep of the voltammetric profiles from pH 1 to pH 5 as presented in Figure 20. The arrow indicates the increase in peak current at ~0.25 V vs RHE with increasing pH value.](image-url)
In addition, the influence of the proton concentration in H$_2$SO$_4$, in which specific adsorption of supporting electrolyte anion occurs, has been investigated. Voltammetric profiles of Ir(111) in H$_2$SO$_4$ solution at different pH values are depicted in Figure 22.

![Voltammetric profiles of Ir(111)](image)

**Figure 22:** Voltammetric profiles of Ir(111) in 0.1 M H$_2$SO$_4$ (blue line), in 0.09 M K$_2$SO$_4$ + 10 mM H$_2$SO$_4$ (red line), in 0.1 M K$_2$SO$_4$ + 1 mM H$_2$SO$_4$ (black line). Scan rate 50 mV/s, Ar-saturated.

The features of the voltammetric profiles at pH 1 were discussed previously in chapter 5.2.1. At pH values of 2 and 3, the ionic strength was kept constant via addition of K$_2$SO$_4$. The charge correlated with the sulfate peak corresponds to 267 µC cm$^{-2}$ at pH 2 and to 272 µC cm$^{-2}$ at pH 3. Taking into account the various sources of uncertainty, it can be affirmed that the charge has a constant value within the pH range, meaning that the sulfate coverage is constant.

5.2.4 **Laser-induced potential transient measurements on Ir(111)**

To clarify the nature of the adsorption processes at the H-upd region, LIPT measurements were performed. LIPT estimates the PME for non-ideal polarizable surfaces like Pt or Ir, thus providing valuable information regarding the M(h k l)|solution interface. By applying short pulses of laser light the temperature of the interface rises suddenly and the change of the surface potential is recorded at constant charge. The sign of this potential transient is mainly determined by the orientation of the water dipoles at the interphase. At potentials below the PME the water dipoles have a positive contribution to the potential of the electrode and the LIPT provides a negative E-t transient. On the other hand, the dipolar contribution is negative at potentials more positive than PME, obtaining positive laser transients. When the applied potential is such that
there is no net dipolar contribution, the intensity of the laser transient obtained is zero. This potential corresponds to the PME and is closely related with the $E_{PZFC}$.

In Figure 23 the potential transients recorded for Ir(111) at pH values from 1 to 5 in perchlorate/fluoride solutions are shown. When the recorded transients are negative, the thermal coefficient of the double layer potential drop is negative ($dE^M/dT < 0$), and the water molecules are oriented with the pair of hydrogens pointing towards the surface. By increasing the applied potentials sufficiently, the magnitude of the laser transient decreases until it reverses sign. When the thermal coefficient is positive the water molecules are preferably oriented with the oxygen towards the surface. Remarkably, in the overall potential window, the laser transient profiles show a monotonous decay after the sharp increase caused by the laser irradiation. This indicates that the recorded transient response results from the double layer reorganization. Non-monotonous responses were observed for Pt and Au, if the rate of the adsorption process is sufficient to compete with the double layer reorganization [56, 119]. Even at more acidic pH values, either at pH 1 or pH 2, the laser transient recorded at low potentials (H-upd region) still shows a monotonic profile. This allows to determine the PME more precisely since no other contribution overlaps with the purely capacitive response. The monotonic laser response recorded on Ir(111) indicates a slower hydrogen adsorption process on Ir(111) than on Pt(111) [56, 120]. This result is in good agreement with the asymmetry of the recorded voltammetric profiles (see Figure 20) as well as with the impedance measurements performed by Kolb et al. [102].
Figure 23: Laser-induced potential transients for Ir(111) at different pH values in HClO₄ with compositions described as in Figure 20. All potentials are versus RHE. Energy beam: 1 mJ/pulse.

Figure 24 shows the laser transients recorded for the same perchlorate/fluoride solutions but at more anodic potentials above the PME. At potentials between 0.40 V and 0.60 V vs RHE the recorded laser transient reverse sign from positive to negative. The second change of the sign of the laser transients was previously observed on Pt(111) at higher potential values [121], indicating that the surface is covered by anions. The presence of anions changes the surface polarization causing a re-orientation of the water molecules. Since neither fluorides nor perchlorates are expected to adsorb specifically onto Ir(111), OH is the species which is likely adsorbed, causing the reversal of the sign during the laser transient. It is remarkable that the change in the laser transient sign takes place at potentials below 0.93 V vs. RHE, the potential value where the broad peak previously assigned to OH adsorption [102] is recorded in the cyclic voltammograms (see Figure 20). Therefore, this result suggests an adsorption of OH occurring at lower potentials than those expected from the voltammetric profile.
Figure 24: LIPT measurements for Ir(111) recorded at potentials above PME in HClO$_4$. The composition of the solutions is as described in Figure 20. Energy beam: 1 mJ. All potentials are referenced to the RHE scale.

The PME is estimated by calculating the temperature coefficient at each applied potential. From the electrocapillary equation [122], using Equation 21, the PME is the potential at which the temperature coefficient of the double layer is zero. To calculate the thermal coefficient from LIPT measurements, linearization of the laser transient data is achieved by plotting them as a function of $1/t^{0.5}$ (see chapter 4.5 for calculation details).

The thermal coefficient was corrected by the thermodiffusion potential using Equation 22. Table 2 summarizes the thermodiffusion potentials of the different employed solutions.
Table 2: Calculated thermodiffusion potentials of the HClO₄ solutions employed for LIPT using the transport numbers calculated from the ionic mobilities at infinite dilution, the latter from ref. [123].

<table>
<thead>
<tr>
<th>Solution</th>
<th>$[\Delta E_{\text{Thermodiffusion}} / \Delta T] / \text{mVK}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M HClO₄ (pH 1)</td>
<td>-0.381</td>
</tr>
<tr>
<td>10 mM HClO₄ + 0.09 M KClO₄ (pH 2)</td>
<td>-0.115</td>
</tr>
<tr>
<td>1 mM HClO₄ + 0.099 M KClO₄ (pH 3)</td>
<td>-0.048</td>
</tr>
<tr>
<td>0.08 M KClO₄ + 0.02 M NaF/HF (pH 4)</td>
<td>-0.030</td>
</tr>
<tr>
<td>(0.1-x) M NaF + x M HClO (pH 5)</td>
<td>0.0264</td>
</tr>
</tbody>
</table>

The solution at pH 1 shows the largest thermodiffusion potential contribution due to the higher mobility of protons compared to the other ions in solution. For pH > 3 the thermodiffusion potential is essentially negligible because of the lower proton concentration. In Figure 25 the $(dE^M/dT)_o$ vs E plots from pH 1 to pH 3 with and without thermodiffusion potential correction are shown. The PME is located at the potential where the line connecting the potential temperature coefficients crosses the X axis.

![Figure 25: Temperature coefficient of the double layer potential with thermodiffusion correction (red squares) and without (black squares) for Ir(111) at pH 1 (A), pH 2 (B) and pH 3 (C), respectively.](image)

The trend of the PME with increasing pH value has then been calculated applying the thermodiffusion correction from pH 1 to pH 5 (Figure 26). The PME shifts 30 mV per pH unit. This result is in contrast to the calculated PME of Pt(111), which remains constant in the SHE scale [121]. Moreover, the estimated PME at pH 0 is extremely low, around 8 mV vs. SHE, whereas the extrapolated PME value of Pt(111) is around 300 mV vs. SHE. This result indicates that, despite the chemical and physical similarity between Pt(111) and Ir(111), their PME values show huge dissimilarities when in contact with aqueous solutions.
It must be highlighted that in the pH range investigated the PME remains inside the previously assigned H-upd region. At acidic pH values, the two peaks in the H-upd region shift until they merge in one peak centered at 250 mV at pH 5. This peak could be related with the sharper one observed in alkaline media (see Figure 19) and assigned to OH adsorption as suggested by Marković et al. [61]. The shift in potential of the hydrogen desorption peak with the increase of the pH value parallels the PME shift. All these experimental observations suggest that the H-upd region (Figure 21) does not only involve hydrogen adsorption but OH adsorption as well.

The interface between Ir(111) and sulfuric acid was also analyzed by means of LIPT to elucidate the influence of sulfate specific adsorption on the restructuration of the water network. Figure 27 shows the laser transients for Ir(111) in contact with sulfate containing electrolytes at pH 1, pH 2, and pH 3. The PME values are located close to the onset of the sulfate peak adsorption which shifts around 30 mV vs RHE per pH unit, as the calculated PME does (see Figure 22 and Figure 27). In this way, it is demonstrated that the sulfate adsorption takes places when the surface is positively charged, thus at potentials above the PME, assuming the correlation between PME and \( E_{PZC} \). The potential transient becomes negative again at ~100 mV at pH 1, ~140 mV at pH 2 and ~170 mV at pH 3 (vs RHE). This potential corresponds to the beginning of the “double-layer” region where sulfates are adsorbed onto the surface [107]. The reversal of the sign of the laser transients, at \( E > \text{PME} \), takes place at much lower potentials in sulfate/sulfuric solutions than in perchlorate/fluoride solutions. This indicates stronger and more
favored sulfate adsorption instead of OH adsorption on Ir(111). Sulfate adsorption causes a strong change of the surface polarization reorienting the water molecules as can be seen by the negative transient in the lower part of Figure 27. A possible reason is the strong interaction between the sulfate adlayer and the water network by hydrogen bond formation, resulting in a reorientation of the water molecules with hydrogen towards the surface. An analogous effect of sulfate adsorption on the water restructuring was previously reported on both Pt(111) and Au(111) electrodes [56, 119].

![Figure 27: Laser-induced potential transients for Ir(111) in contact with (A) 0.1 M H₂SO₄, (B) 0.01 M H₂SO₄ + 0.09M K₂SO₄, and (C) 1 mM H₂SO₄ + 0.1 M K₂SO₄. PME values are highlighted bold red in the upper part of the figures. Energy beam: 1 mJ. All given potentials are referenced vs. RHE.](image)

In order to gain more insights of the pH influence on the interfacial properties of Ir(111), LIPT were also performed in alkaline solution. Figure 28 shows the laser transient for the Ir(111) electrode in a 0.1 M NaOH solution.
The PME calculated is 0.28 V vs. RHE, confirming that the peak at 0.3 V is caused by OH adsorption, as suggested by CO-displacement experiments [61]. This PME value does not follow the PME-trend calculated in Figure 26 (increase of PME potential of ~30mV/pH unit). This observation could be a starting point for the investigation of the PME-trend as a function of the OH concentration in alkaline solutions.

5.2.5 Potential of zero total charge of Ir(111)

In order to gather supplementary information about the nature of adsorption-desorption processes at the interface, CO-displacements experiments for the identification of the $E_{PZTC}$ were realized. CO-displacement experiments performed by Kolb et al. [102] in 0.1 M $H_2SO_4$ demonstrated that the $E_{PZTC}$ is located at the center of the sulfate peak. On the other hand, as reported before, the voltammetric profiles in perchloric acid are not yet fully understood and CO-displacement experiments can lead to a better comprehension of their features.

After the CO-displacement experiments, when the surface is recovered to the initial state via CO stripping, CO oxidation takes place on Ir(111) at less positive potentials than on Pt(111) (see Figure 29). The CO oxidation is observed at ~720 mV vs. RHE on Ir(111) in 0.1 M $HClO_4$ solution and on Pt(111) at 800 mV vs. RHE (inset Figure 29).
Ir and Pt have similar atomic sizes (0.272 and 0.278 nm, respectively), therefore comparing the adsorption of CO at Pt(111) and Ir(111) can provide useful insights into the electronic effects of surfaces on the interfacial structures. In fact, the comparison of the same crystallographic plane allows decoupling between geometric and electronic effect. Thus, for Pt(111) and Ir(111), the difference in activity can be attributed solely to the difference in electronic structure between the two electrocatalysts. On the other side, it is well known that the mechanism of CO oxidation involves adsorbed OH [124, 125]. In both Ir(111) and Pt(111) the CO oxidation happens on a metal surface where OH is specifically adsorbed. Therefore the highest catalytic activity of Ir(111) for CO oxidation results from the adsorption of OH on Ir(111) at lower potentials as compared to Pt(111). A decrease of the overpotential for CO oxidation is the consequence, in agreement with previous results obtained by LIPT which located the PME at low potentials (see Figure 23). For the coulometric estimation of CO coverage, the charge upon integration of the CO oxidation peak was corrected for the charge of the current-potential profile measured in the absence of chemisorbed CO, according to the procedure described by Weaver et al.
The charge of the current-potential profile is obtained by the integration between the $E_{PZTC}$ and the upper limit of the potential excursion during CO stripping. The CO oxidation charge obtained was $295 \, \mu C \, cm^{-2}$ in 0.1 M HClO$_4$, slightly lower than the reported literature values of $300 \, \mu C \, cm^{-2}$ [126, 127]. This value corresponds to a CO coverage of $\Theta = 0.59$ as compared to the reported values of $\Theta = 0.6$. Figure 30 depicts CO oxidations on Ir(111) for pH 2, pH 3, and pH 4.

![Figure 30: CO-oxidation experiments at (A) pH 2, (B) pH 3, (C) pH 4 in HClO$_4$. The solutions are as described in Figure 20. Scan rate 20 mV/s.](image)

The reported $\Theta$ at pH 1 is consistent with the coverage measured upon CO stripping in 10 mM HClO$_4$ + 0.09 M KClO$_4$ solution (pH 2), namely $295 \, \mu C \, cm^{-2}$. In 1 mM HClO$_4$ + 0.099 M KClO$_4$ (pH 3), and in 0.08 M KClO$_4$ + 0.02 M NaF / HF (pH 4) the charge obtained upon stripping was slightly higher: $312 \, \mu C \, cm^{-2}$, and $324 \, \mu C \, cm^{-2}$, respectively. The charge measured in the amperometric profile recorded at constant potential during CO adsorption corresponds to the difference between the charge density on the CO-covered and the CO-free surfaces:

$$q_d = q_{m/CO} - q_{m}$$  \hspace{1cm} (Equation 24)

where $q_d$ is the charge displaced during the potentiostatic adsorption of CO, $q_{m/CO}$ is the charge density of the CO-covered electrode and $q_m$ is the charge density of the CO-free surface. The double layer capacitance of the CO-saturated Ir(111)-aqueous interface as measured by cyclic voltammetry is markedly smaller than that observed in the absence of CO (see Figure 29 and Figure 30). Thus, as a first approximation, $q_{m/CO}$ is negligible [128]. Figure 31 depicts the charge displaced at 0.15 V and 0.3 V vs. RHE in 0.1 M HClO$_4$. The value of $q_d$ is positive at potentials below the $E_{PZTC}$, due to the displacement of $H_{ads}$ by CO. At 0.3 V vs. RHE, negatively charged
species are leaving the surface, indeed indicating that OH is adsorbing at the anodic peak centered at ~0.25 V.

![Figure 31: Charge displaced by CO chemisorption on Ir(111) in 0.1 M HClO₄ at (A) 0.15 V and (B) 0.3 V. CO introduced in the electrochemical cell after ~60 s in (A) and after ~45 s in (B).](image)

The displaced charge can therefore be approximated to the inverse of the charge density at the metal surface (\(q_d = -q_m\)). \(q_m\) corresponds to [129]:

\[
q_m = \sigma - F \Gamma_H + F \Gamma_{OH}
\]

(Equation 25)

where \(\sigma\) is the charge situated on the metallic side of the double layer (so called free charge density), \(\Gamma_H\) the thermodynamic excess of adsorbed hydrogen and \(\Gamma_{OH}\) the thermodynamic excess of adsorbed OH. For a high coverage of adsorbed species, the extent of the contribution of hydrogen and OH adsorption prevails over the contribution of the free charge density, thus strongly influencing the value of \(q_m\). However, the magnitude of the thermodynamic excess of adsorbed species cannot be measured in aqueous solutions [129]. As can be deduced from Equation 25, hydrogen adsorption “compensates” a positive \(\sigma\), and OH adsorption a negative \(\sigma\). Consequently, the \(E_{PZTC}\), being the potential at which \(q_m = 0\), shifts to a lower potential when the amount of adsorbed OH is higher than that of hydrogen. As can be observed in Figure 21, the co-adsorption the two species do not allow for a deconvolution in two different adsorption peaks representing hydrogen and OH adsorption, respectively. Thus, the coverage of hydrogen and OH species is not easy to estimate due to the overlapping of the two processes. Figure 32 depicts the voltammetric profiles of Ir(111) from pH 1 to pH 4 and the charge curves obtained from the integration of the corresponding voltammogram with the use of the charge displaced by CO at 0.3 V as integration constant and considering \(q_{m/CO}\) negligible (see Equation 24). The co-adsorption of hydrogen and OH takes place in the potential region where the \(E_{PZTC}\) is located.
For the sake of comparison, Figure 33 depicts only the charge curves obtained from pH 1 to pH 4 from the integration of the cyclic voltammograms with the use the charge displaced by CO at 0.3 V as integration constant (see Equation 24).

Figure 32: Voltammograms of Ir(111) at (A) pH 1, (B) pH 2, (C) pH 3, (D) pH 4. Solutions employed are as described in Figure 20(A) and (B), scan rate 50 mV/s. Red dotted lines represent the charge density curves obtained from the integration of the cyclic voltammograms with the use the charge displaced by CO at 0.3 V as integration constant (see Equation 24).

For the sake of comparison, Figure 33 depicts only the charge curves obtained from pH 1 to pH 4 from the integration of the cyclic voltammograms with the use the charge displaced by CO at 0.3 V as integration constant.
5.2.6 Comparison of EPZTC and PME

The EPZTC and PME values as a function of the pH value are compared (see Figure 34). EPZTC increases slightly with the increase of the proton concentration (~7 mV/dec). The increase in EPZTC with the increase of the pH value indicates a compensation of the negative free charge of the metal by the positive charge due to higher OH coverage. Based on Equation 25 and on the fact that the EPZTC is higher than the PME, it can be deduced that the surface excess of hydrogen is higher than that of OH at the EPZTC. For the four different pH values, the EPZTC is situated in the H and OH co-adsorption region always before the peak at ~0.25 V vs RHE corresponding to OH adsorption. In addition, the nature of the latter is confirmed by the fact that the potential difference between PME and EPZTC increases as the pH value decreases. As explained above, at EPZTC, the surface excess of hydrogen is higher than that of OH, and the H/OH adsorbates ratio is reduced as the pH increases.

Figure 33: Charge curves obtained from the integration of the cyclic voltammograms, with the use the charge displaced by CO at 0.3 V as integration constant. Inset: zoom of the curves at E ≈ EPZTC.
Water dipoles are strongly affected by the electrostatic force with the free charge density on the surface, therefore the potential of reorientation of the water is closely related to the $E_{PZFC}$. However, the net orientation of the water dipole is affected also by the chemical interaction between water and metal surface, in particular in case of transition metals where specific adsorption of H and OH takes place. Unfortunately, the magnitude of the electrostatic force and of the chemical interaction between water and metal cannot be decoupled in aqueous solutions. The water/metal chemical interaction is crucial because it can orientate water even without an applied electrical field, shifting the PME to lower potentials.

The PME has been shown to be located close to the $E_{PZFC}$ in the case of mercury [130, 131], gold [119, 132], and Pt(111) [84]. For Ir(111), due to charge-transfer processes, the surface cannot be considered ideally polarizable, and the conclusions drawn for mercury and gold cannot be transferred to the metal under investigation in the present work. In the total absence of influence of adsorption processes on the $E_{PZFC}$, this should be constant and shift 60 mV in the RHE scale. The fact that shift 30 mV indicate that adsorption processes affect the distribution of free charges at the interphase. In fact, in case of Ir(111) the direct measurement of the $E_{PZFC}$ is precluded by the hydrogen and anion adsorption reaction. For Pt(111), which specifically adsorbs H and OH like Ir(111), the extrapolation of the $E_{PZFC}$ from the $E_{PZTC}$ has been performed via further calculations which required the knowledge of the $E_{PZC}$ of the CO covered surface inferred from UHV measurements [56]. The UHV based estimation of the $E_{PZC}$ of Ir(111) is a value not yet available for the Ir(111)-CO surface.

Figure 34: $E_{PZTC}$ (black dots) and PME values corrected for the thermodiffusion coefficient (red dots), as a function of the pH value in HClO$_4$. The composition of HClO$_4$ solutions is as described in Figure 20.
5.2.7 Electrolyte influence on the work function

Both LIPT and CO-displacement measurements have shown a significant influence of the solvent on the restructuring of the double layer, thus modifying the interfacial properties of Ir(111). Here, the specific nature of the anion has to be considered as it plays an important role in the redistribution of the charge across the interface (either OH or sulfate). In particular LIPT has provided PME values consistently lower for Ir(111) than for Pt(111). This trend qualitatively agrees with the work function values of both metals, but the potential differences between the Ir(111) and Pt(111) PMEs are higher than the difference between their work functions values ($\phi^M$). The calculated $\phi^M/e$ of both Pt(111) and Ir(111) in vacuum conditions differs between 70 - 200 mV, according to references [133, 134]. However, as demonstrated (see Figure 35), the difference between their calculated PME in aqueous solution and $\phi^M$ values is higher and this difference increases with the pH value. For comparison, in Figure 35 the linear variation of the PME of Ir(111) with the pH value is plotted compared with that for Pt(111) in the RHE scale [121].

![Figure 35](image)

**Figure 35:** PME fitted trends calculated from this work (for Ir(111)) and from Garcia-Araez et al. [121] (for Pt(111)) vs the logarithm of proton concentration in solution. The difference in the work functions of Pt(111) and Ir(111) in vacuum is also shown for the sake of comparison.

In order to understand the observed discrepancy between the PME values and metal work functions of both Pt and Ir metals, especially when the pH value is increased, it is convenient to consider the different contributions to the electrode potential in the absence of specific ion adsorption [79]:

$$E^M = \phi^M/e + \delta \chi^M + g^S(dip) + g^M(ion) - E_{abs(ref)}$$  \hspace{1cm} (Equation 26)
where $\Phi^M$ is the work function of the clean metal surface, $e$ is the electronic charge, $\delta \chi^M$ is the change in the surface electronic (“electron spillover”) contribution to $\Phi^M$ caused by contact with the solvent, $g^s(dip)$ is the surface potential component due to the net solvent dipole orientation, $g^s_M$ (ion) is the contribution from “free” charges, associated with excess electronic charge on the metal surface along with the ionic double-layer countercharge, and $E_{\text{abs}}(\text{ref})$ is the so-called “absolute” potential of the reference electrode. While the main contribution to the thermal coefficient results from the double layer, other terms might also affect it. One of them is the thermal coefficient for the electrode work function, whose value is usually very small, e.g. $\approx 0.15 \text{ mV/K}$ for Pt(111). For Ir(111) the $\phi^M$ did not show any significant temperature dependence, even though the exact value of the thermal coefficient for the work function could not be estimated because of large error bars [133]. The potential of zero charge can be obtained from Equation 26 considering that $g^s_M$ (ion) = 0:

$$E_{\text{PZC}} = \phi^M/e + \delta \chi^M + g^s(dip) - E_{\text{abs}}(\text{ref})$$

(Equation 27)

The $g^s(dip)$ contribution is often regarded as constituting the major solvent influence on $E_{\text{PZC}}$, but the interfacial electron density profile (i.e., the $\delta \chi^M$ term) is also modified by the solvent-induced contribution. Although the contribution of the solvent on the potential seems to have a crucial effect, the calculation of the magnitude of $\delta \chi^M$ as well as $g^s(dip)$ requires an understanding of solvent-induced changes on local surface potentials which has not yet been achieved. As demonstrated for Pt(111) using UHV-based studies of solvation-induced $\Phi^M$ changes at suitably low temperatures, the influence of both $\delta \chi^M$ and $g^s(dip)$ terms for Pt(111) is important [135]. The large (ca. 1 eV) $\Phi^M$ decrease measured on Pt(111) in UHV upon dosing water can therefore be attributed to significant contributions from both the $g^s(dip)$ and $\delta \chi^M$ terms [136]. CO charge displacement data, combined with the known $\Phi^M$ value for Pt(111), 5.9 eV, by means of Equation 27, suggests a large negative interfacial solvent contribution to the electrode surface potential. In the case of Ir(111) there is no UHV-based study of solvation-induced $\Phi^M$ changes. However, based on the results obtained in this work, for both metals the relative contribution of $g^s(dip)$ and $\delta \chi^M$ to the PME can be compared as a function of the pH value. When the pH value increases, even in absence of an electric field, the magnitude of the chemical interaction between H$_2$O molecules and electrode surfaces is described by a linear correlation having different slopes for Ir(111) and Pt(111). These observations would agree with the highest oxophilicity of Ir compared
with Pt reported by Marković et al. [61], since a stronger interaction of the Ir(111) with the solvent is expected from the obtained results.

5.3 Electrolyte composition influence on electrochemical oxidation

In the previous chapters, the effect of the electrolyte composition on the electrochemical interface was investigated in the potential region where reversible processes are occurring. The focus of the next chapters is the influence of the electrolyte on the irreversible oxidation of both Ir(111) and Pt(111) single crystals.

5.3.1 Anion effect on electrochemical oxidation of Ir(111)

In sulfuric acidic solutions the influence of sulfate anions on the voltammetric profile of Ir(111) has been already evidenced (see Figure 22). Their specific adsorption on Ir(111) surface is expected to have also an influence on the oxidation process of the metallic surface. Anodically formed Ir oxide films (AIROF) were grown by means of potential cycling between 1.575 and 0.7 V (vs RHE). The lower potential limit for the AIROF growth was selected to avoid aging, occurring when the oxide film is reduced at negative potentials [137]. The mechanism of the Ir-oxide growth in sulfuric acid solution will not be explained in detail as it has been extensively investigated before [138–141]. To summarize, the current hypothesis of the mechanism is that the anodic oxidation of Ir takes place on the surface via chemisorption of OH radicals (*OH) and O atoms (*O). According to Mozota et al. [142], a monolayer of *OH adsorbs on the surface of Ir at potentials between 1.1 and 1.2 V vs. SHE in sulfuric acid solution, whereas a monolayer of *O atoms forms between 1.4 to 1.5 V vs. SHE. In HClO₄ solution the potential of chemisorption of *OH and *O is still a controversial issue, as explained in chapter 5.2. In 0.1 M HClO₄, the adsorption of *O and the consequent formation of Ir-oxide can be seen distinctively in the first anodic scan after cycling the electrode up to a potential of ~1.45 V vs RHE. The influence of either the perchlorate and sulfate anions on the oxidation potential of the Ir(111) is shown in Figure 36, where a detail of the first anodic scan for 0.1 M HClO₄ and 0.05 M H₂SO₄ oxidation is represented. The specific adsorption of sulfate anions at the interface hinders the oxidation of the metallic surface, shifting the oxidation peak to more positive potentials.
The AIROF film thus formed shows distinctive voltammetric features associated with the change in the oxidation state of Ir. In Figure 37 the oxidation-reduction peaks are associated with the following reaction [137]:

\[
(IrO_2*nH_2O)_5 + 5e^- + 7H_3O^+ + 2(X^-) \rightleftharpoons [Ir_5O_3*(OH)_7*5nH_2O)]^{2+}(X^-)+7H_2O \quad (Equation \ 28)
\]

where \(X^-\) is the anion present in solution.

The influence of the anion on the stoichiometry of the Ir(III) / Ir(IV) conversion reaction was confirmed via nanogravimetry measurements performed with an electrochemical quartz crystal microbalance [139]. During the Ir(III) / Ir(IV) conversion reaction, both protons and anions are expelled from the oxide during oxidation (and injected during reduction), while the ratio between them is determined by the pH value and the ionic strength. Furthermore, the presence of sulfate anions on AIROF has been suggested using results obtained via X-ray Photoelectron Spectroscopy [140]. The influence of the anion on the Ir(III) / Ir(IV) reaction is shown in Figure 37:
Figure 37: (A) Anodic and (B) cathodic voltammetric peaks associated with the redox transformations described in Equation 28. Scan rate 50 mV/s, O\textsubscript{2}-saturated solution. From ref. [143].

As can be seen in Figure 37 sulfate anions, due to their stronger affinity to Ir, influence the redox process, reducing the potential gap between reduction of Ir(IV) and oxidation of Ir(III).

5.3.2 Electrochemical oxidation of Pt(111)

In fuel cells application, improving the activity and stability of the catalyst is the main challenge. Pt is one of the most active electrocatalyst for the ORR and HOR and thus is in the spotlight of the state-of-the-art materials in fuel cells. [144]. Pt surface oxidation strongly affects both its activity and durability, and is thus one of the issues causing a decreasing efficiency in fuel cells [145, 146]. In fact, even though a fuel cell typically operates under almost steady-state conditions below 1.0 V, the catalyst on the cathode side can be oxidized. Oxidation occurs during start-up or shutdown of the fuel cell, a process during which the cathode can reach potentials up to 1.5 V [147].

The mechanism of Pt dissolution is still not clear, as Pt can dissolve anodically as a result of oxide formation, cathodically during oxide reduction, or by chemical dissolution of the formed oxide. An experimental study by Topalov et al. [148] indicates that formation and reduction of subsurface oxides at high potentials rather enhances Pt dissolution probably through dynamic surface reconstructions. Therefore, the amount of Pt oxides need to be appropriately diminished during fuel cells operations to enhance the cathode durability. A suitable control of Pt stability can be achieved by a deeper understanding of Pt-oxide formation and reduction mechanisms.

The electrooxidation of Pt has been intensively studied in the past 50 years [146, 149–152]. Since early works, the hysteresis observed between oxidation and reduction scans of
polycrystalline Pt led to the formulation of a place-exchange process [150, 153], whose scheme is depicted in Figure 38:

![Figure 38: Scheme of place-exchange process on Pt caused by OH adsorption. From [153].](image)

However, these studies have been conducted on polycrystalline Pt, i.e. on inhomogeneous surfaces, which invalidates the assumption of uniform geometry that is the basis of many interfacial studies. Therefore, a study on single crystals with a defined structure such as Pt(111) can improve current understandings of the process. Furthermore, the surface oxidation is a highly structure-sensitive process, an investigation on Pt(111) single crystal enables to cast more light into its oxidation kinetics. Place-exchange mechanism and oxidation kinetics of Pt(111) in acidic solution have been studied extensively [154–157], but these processes have not yet been extensively characterized in alkaline solution.

In this chapter, investigation upon oxidation kinetics and surface reorganization has been performed via cyclic voltammetric experiments. In Figure 39, the voltammetric profile of Pt(111) in 0.1 M NaOH (black dotted line) from 0.05 V to 0.9 V vs RHE is shown together with consecutive oxidation CVs up to 1.5 V vs RHE. The characteristic voltammetric profile of Pt(111) in alkaline medium involves three potential regions: i) between the beginning of the HER and 0.35 V assigned to hydrogen adsorption/desorption; ii) a featureless region with small current between 0.35 and 0.6 V attributed to double-layer charging; and iii) the adsorption/desorption of hydroxide anions centered at 0.75 V [145, 158]. At potentials above 0.9 V the asymmetric shape of the CVs indicates irreversible surface oxidation. Upon oxidation and reduction, dynamic surface reconstructions can be clearly observed from the growth of the A1 and A2 peaks, representing {110} and {100} defects, respectively [156, 157].
Figure 39: Cyclic voltammograms of electrooxidation of Pt(111) in Ar-saturated 0.1 M NaOH. Black dotted curve represents the voltammetric profile of Pt(111) before oxidation. Scan rate 50 mV/s. \( A_1 \) and \( A_2 \) voltammetric features correspond to \{110\} and \{100\} defects, respectively.

The effect of different anodic limit potentials on the growth of the \{110\} and \{100\} defects and their charge evolution upon cycling can elucidate the place-exchange process [154].

In Figure 40 the normalized charges of \( A_1 \) and \( A_2 \) during oxidation are plotted as a function of the number of cycles.

Figure 40: Normalized integrated charge for (A) \{110\} and (B) \{100\} defects as a function of the number of cycles. Black squares, red circles and blue triangles represent CVs performed up to 1.4, 1.5, and 1.6 V vs. RHE, respectively.
The charge related to \{110\} defects increases monotonically with sequential cycling for experiments performed up to different anodic limits. The charge involved in \{100\} defects increases more rapidly as compared to the \{110\} ones, and then slightly decreases as the number of cycles increases. It appears that the reaction scheme coincide with the scheme representing the place-exchange process of Pt(111) in sulfuric acidic solutions formulated by Björling et al. [154, 156] as represented in Figure 41:

![Reaction scheme for the quantification of the place-exchange process of Pt(111) in sulfuric solutions. X represents \{111\} terraces, Z the \{110\} steps, Y the \{100\} steps, and \(k_1, k_2, k_3, k_4\) are the reaction constants. Scheme taken from [154].](image)

Experimental data in sulfuric acidic solution show the initial growth of \{100\} steps, which are then converted in \{110\} defect sites. This model was confirmed also in perchloric acid solutions by Gómez-Marín et al. [155]. The data fitting to the same model could not be performed in alkaline solution. In fact, the obtained data were not sufficient to confirm or discard the model of defect-growth as proposed for acidic solutions due to the limited amount of experiments and cycles performed.

The asymmetricity of the voltammetric profiles upon oxidation appears in CVs of single crystal as well as in polycrystals and nanoparticles [159]. In Figure 42, details of the corresponding oxidation and reduction regions are depicted. \(A_{\text{OH}}\) represents the reversible adsorption of hydroxide anions and the peak at 1.02 V (denoted as \(A_O\)) represents the irreversible surface oxide formation [160, 161]. The oxide growth causes a shift in the potential of the hydroxide adsorption (\(A_{\text{OH}}\)) and oxide reduction (\(A_{R1}, A_{R2}, A_{R3}\)) peaks. Another proof of the oxide growth process is the decrease in intensity of \(A_O\) due to the increasing amount of surface oxide.
The $A_{R3}$ peak corresponding to PtO reduction shows strong irreversibility. Upon fitting of its peak potential at different scan rate, insights into the PtO reduction kinetics were obtained (see Figure 43B). The voltammetric experiments at different scan rates are shown in Figure 43A.

Figure 43: (A) 10th voltammetric oxidation cycle up to 1.5 V at different scan rates. (B) Linear fitting of the logarithm of scan rate vs E of $A_{R3}$ to determine the kinetic of PtO reduction.

Upon fitting the $A_{R3}$ peak potential as a function of $\upsilon$, a “Tafel” slope of 0.038 V was determined (see Figure 43B). This value is close to 0.04 V, the Tafel slope corresponding to a two-stage oxide reduction electrochemical process in which the second stage is the rate-determining step, and the first stage is at quasi-equilibrium [162, 163].
In addition, a study on the influence of Cl$^-$ adsorption on the place-exchange and oxidation processes has also been performed. The analysis of the oxidation/reduction process with different NaCl concentrations was conducted. Cl$^-$ is competitively adsorbed with OH$^-$ on Pt surfaces and is expected to have an influence on the rate of oxidation and on the place-exchange process. As can be seen from Figure 44, the oxidation / reduction cycles until 1.5 V vs RHE in 0.1 M NaOH + 0.01 M NaCl do not show any difference when compared with the voltammograms in Figure 39.

![Figure 44: Cyclic voltammograms of electrooxidation of Pt(111) in Ar-saturated 0.1 M NaOH + 0.01 M NaCl. Black dotted curve represents the voltammetric profile of Pt(111) before surface oxidation. Scan rate 50 mV/s.](image)

Cl$^-$ ions do not show an influence on the reversible Pt-OH adsorption process and on the irreversible oxidation of the surface, as observed previously by Marković et al. [161]. Investigation of the Cl$^-$ influence on the place-exchange process in alkaline solutions at pH 12 and pH 13 was also realized. The analysis of the charge associated to {110} and {100} defects grown upon cycling up to 1.5 V has been carried out (see Figure 45 for charges associated to {110} and {100} defects at pH 12).
The plot of {110} and {100} defects charges of a Pt(111) electrode in Cl\textsuperscript{-} containing solution did not show any difference with respect to the solution without Cl\textsuperscript{-} ions (black squares in Figure 45) either at pH 12 or at pH 13 (the latter not shown). Consequently, it can be concluded that the presence of Cl\textsuperscript{-} ions in the electrolyte influences neither the Pt oxidation/reduction nor the place-exchange process in alkaline solutions.

**5.4 Electrolyte composition influence on gas evolution reactions**

**5.4.1 Influence of alkali cations on HER on Pt(111) in H\textsubscript{2}SO\textsubscript{4} solution**

In sulfuric acid solutions, the Pt(111) system has been previously analyzed within the potential region where (bi)sulfate anions are specifically adsorbed at the surface. At these potentials not only the nature of the alkali cations but also electrochemical properties of the anions contributed to the performance of the surface active sites. In the following, important model reactions taking place outside of this region are considered, namely HER and HOR.

The activity of metal catalysts for the HER reaction can be described using a *H-binding adsorption energy descriptor as represented in the volcano plot in Figure 3. The HER takes place at potentials which are more negative than the $E_{FZC}$ of Pt. Therefore, anions are not expected to be specifically adsorbed on the surface. For example, in HClO\textsubscript{4} solution perchlorate anions do not specifically adsorb on the Pt surface in a wide potential window [155]. On the other hand, in
H₂SO₄ solutions the (bi)sulfate layer is desorbed from the surface at ~0.3 V vs RHE, i.e. at higher potentials than the onset of the HER. It has been shown in Figure 12 that the nature of the anions (either sulfate or perchlorate) as well as the ionic strength of the electrolyte do not significantly affect the HER and the HOR under the given experimental conditions. In fact, after iR correction Pt(111) reveals similar HER activity in both H₂-saturated 0.05 M H₂SO₄ and 0.1 M HClO₄ electrolytes.

In contrast, the presence of alkali metal ions can significantly influence these two reactions, as well as the base voltammetry of Pt(111) electrodes (as shown in Figure 16). As can be seen from Figure 3, the Pt(111) surface locates close to the activity optimum in terms of H-binding energy for the HER and HOR. To reach the optimum, surface active sites should bind the reaction intermediates slightly weaker than those related to Pt(111). A possible method to change the binding energies of H-intermediates would be the tuning of the electrolyte composition. However, the presence of alkali cations in sulfuric acid solutions only slightly change the observable H-adsorption/desorption region (see Figure 16). Hence, one can expect that there will be no significant influence on the HER and HOR activity. On the one hand, it is expectable that any positively charged species in the electrolyte might still influence the catalytic performance of the electrodes below the E_pzc. Nevertheless, under common consideration, the possible influence of positively charged ions in the electrolytes on the electrocatalysis of HER and HOR is normally not taken into account.

From Figure 46, it is evident that the nature of the cations influences the activity of both HER and HOR. However, there is no linear correlation between the activities and the fundamental properties of alkali metal cations in the series from Li⁺ to Cs⁺. In a K⁺-containing electrolyte noticeably low activities of the Pt(111) electrodes are obtained, while the HER and HOR activities are the highest in the Rb⁺-containing electrolytes. It is important to emphasize that due to relatively high cathodic currents caused by the HER, even small errors in the determination of the uncompensated resistance by means of EIS would result in large errors in the activity assessment. Therefore, Figure 46C also shows a bar chart comparing the non-corrected activity data related to the HER currents measured at a potential - 0.06 V vs RHE. From Figure 46B and C one can observe that the activity trend remains the same irrespective to the iR-correction.
Figure 46: (A) Typical RDE-voltammograms (iR-corrected) in the HER-HOR potential region observed for Pt(111) electrodes in H$_2$-saturated 0.05 M H$_2$SO$_4$ + 0.05M Me$_2$SO$_4$ (Me = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) electrolytes and for Pt(polycristalline) electrode in H$_2$-saturated 0.05 M H$_2$SO$_4$. (B) details from Figure 46A of the HER at low overpotential. (C) Bar chart comparing the corresponding measured HER activities without iR correction: even in this case the activity trends remain the same. Figure 46C from ref. [110].

It is extremely difficult to draw definitive conclusions about the origin of the observed catalytic trends within the current theoretical framework. In fact, the cyclic voltammograms shown in Figure 16 do reveal slight changes in the adsorption/desorption of hydrogen at the surface in different electrolytes, but the changes are not consistent with the trends detected in the activity for HER and HOR. One relevant observation from Figure 46 regards the activity for both HER and HOR in Rb$^+$ containing electrolyte at a Pt(111) electrode. The voltammogram is almost
exactly the same as the one at the polycrystalline Pt electrode (black dotted line). This result proves that the tuning of the electrolyte composition could be as an effective strategy as changing of the electrode surface properties to achieve improved electrocatalytic performance. In Figure 47 the comparison of the HER on Pt(111) and Pt(pc) is shown.

Figure 47: Chronoamperograms taken at -0.06 V, 1600 rpm, in H₂ saturated 0.1 M HClO₄ comparing the activity of Pt(polycrystalline) and Pt(111) towards HER. From ref. [143].

5.4.2 Alkali metal cations influence on OER on Pt(111) in H₂SO₄ solution

Another model electrocatalytic reaction which takes place outside the (bi)sulfate adsorption/desorption potential region of Pt(111) is the OER. OER normally takes place on oxidized electrodes, and the properties of these surfaces are significantly different as compared to the corresponding metallic ones. Pt(111) electrodes form thin oxide films at the surface prior to the OER in acidic media. The Pt oxide thus formed is not a great catalyst for the OER, as it binds oxygen containing intermediates too weakly (see volcano plot in Figure 4). However, model surfaces such as Pt oxide formed upon oxidation of Pt(111) can provide useful insights into the role of the electrolyte components for the OER. Thus, several experiments were performed to investigate how the electrocatalytic properties of electrochemically formed thin Pt oxide films at the surface of Pt(111) electrodes are influenced by the nature of the alkali metal cations in sulfuric acidic solutions.

It should be noted that it is known that sulfate anions desorb from the surface of the Pt(111) electrodes before the onset potential for the OER. However, they likely remain in close proximity to the electrode to compensate the net positive charge of the surface of the electrode. Furthermore, the nature of the alkali metal cations should not change the OER activity due to a positive net charge of those electrodes. Expectations would be therefore that the alkali cations do
not influence OER as the perchlorate and sulfate anions do not influence the HER. However, Shao-Horn et al. [43] have demonstrated recently that alkali metal cations do influence the properties of the active sites at the surface of the O₂-evolving electrodes in alkaline media, though the effect is not as pronounced as in the case of the ORR [44]. The alkali metal cations influence on the catalytic activity of Pt was confirmed also for the CER [49]. As shown in Figure 48 for Pt electrodes in sulfuric acid, the OER activity changes only slightly in Li⁺, Na⁺, K⁺ and Cs⁺ containing electrolytes (both with or without iR-correction). Notably, the Rb⁺ containing electrolyte shows a rather unexpected exception with a reproducible and significant increase in the catalytic activity of the electrodes towards the OER.

![OER voltammograms on Pt(111) electrodes in O₂-saturated 0.05 M H₂SO₄ + 0.05M Me₂SO₄ (Me = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) electrolytes. (B) Bar chart comparing OER-activities at 1.82 V, from ref. [110].](image-url)

The activity of the Pt(111) electrodes was noticeably and systematically higher in presence of Rb⁺ for electrocatalytic reactions as HER and OER which are governed by different descriptors. This behavior seems interesting since little literature is available which can explain this effect. Rb⁺ ions are normally excluded from systematic investigations in electrocatalysis and seldom used in industry, despite of the fact that it is as abundant as e.g. Cu. It can be speculated that non-specifically adsorbed Rb⁺ ions cause a destabilization of the water molecule layer adsorbed at the surface, thus changing the energy barrier necessary for H⁺ and OH⁻ to be reduced and oxidized, respectively. The origin of this experimentally observable activity enhancement is still not clarified from a purely electrocatalytic point of view. One difference of the Rb⁺ ion with respect to the other alkali cations is the relevant presence of a radioactive isotope. In fact, Rb⁺ contain up to 28% of the beta-radioactive isotope ⁸⁷Rb [164], which undergoes a natural β⁻ decay.
The effect of radioactive isotopes in promoting some heterogeneous reactions was already documented several decades ago [165–168], but it has relatively rarely been the subject of systematic investigations in electrocatalysis. Nevertheless, this underlines the importance of investigation of the vast unexplored horizon of electrocatalysis in terms of both theoretical and experimental aspects. However, from the experimental data available, no trend connecting physico-chemical properties of the alkali cations to their influence on the OER activity for the Pt(111) electrode could be discerned.

5.4.3 Anions influence of OER on AIROF

The effect of the electrolyte composition was also investigated for the OER at model Ir-oxide electrodes. As can be seen from the volcano plot in Figure 4, Ir oxide is the state of the art electrocatalyst for OER in acidic solutions. Iridium oxide thin films were electrochemically grown on a Ir(111) surface as explained in chapter 5.2.3.

The pH dependence of the OER for AIROF in different electrolytes (such as phosphate and sulfate) has been investigated by Burke et al. [169], showing that it exhibited a traditional behavior with a potential change of 59 mV per pH unit. The effect of different anions present in the supporting electrolyte on the rate of the OER on electrochemically oxidized polycrystalline Ir samples has also been studied, using sulfuric, perchloric, and phosphate solutions [170]. However, since the comparison for the OER has been performed in solutions with effectively different pH values, it is difficult to extract a direct comparison of the influence of the anions on the OER kinetics. In Figure 49 the comparison of the OER activities of AIROF growth onto Ir(111) crystal in perchloric and sulfuric acid solution is shown.

As can be seen in Figure 49, HSO$_4^-$ ions, which are present in the electrolyte, significantly hinder the OER, as expected from the discussion in the chapter about the Ir(111)-oxidation process. The Tafel plot in Figure 50 confirms the influence of the spectator anions on the kinetics of the OER. In fact, the fitting of the CV in the linear region resulted in a lower Tafel slope for HClO$_4$ with respect to the H$_2$SO$_4$ solution, i.e. 49 mV/dec and 56 mV/dec respectively. The stronger affinity of the sulfate anions to the Ir as compared to the perchlorate anions decisively affects the electrocatalytic activity of AIROF and underlines once more the influence of “spectator” species of the electrolyte on the electrocatalytic reactions.
Figure 49: OER activities of Ir-oxide thin films in O$_2$-saturated 0.1 M HClO$_4$ and 0.05 M H$_2$SO$_4$ (the curves are iR-corrected). Scan rate 50 mV/s.

Figure 50: Tafel plot of OER on AIROF as represented in Figure 49. The experiment has been performed in O$_2$-saturated 0.1 M HClO$_4$ and 0.05 M H$_2$SO$_4$ solutions.

Figure 51 compares the results obtained in this work and those which are reported as state-of-the-art in the literature and obtained under similar conditions for AIROF film electrodes. The results are not compared to the literature activities measured using iridium oxide nanoparticles because there is a high uncertainty associated with the estimation of their electrochemically active surface area, which could lead in turn to an erroneous estimation of the activity. However, the highest activity obtained for Ir oxide nanoparticles is also indicated in Figure 51.
Figure 51: Tafel plots comparing the geometrical current densities (in logarithmic scale) vs over-potential for the OER on Ir-oxide films. Green and black lines show data adapted from [171] (OER on AIROF measured in 0.5 M H$_2$SO$_4$) and from [172] (first scan of OER on polycrystalline Ir measured in deaerated 0.1 M HClO$_4$). Red and blue lines: OER activities measured in this work for AIROF in 0.1 M HClO$_4$ and 0.05 M H$_2$SO$_4$, respectively. The purple spot corresponds to Ir-oxide powders as measured in [34] in 1 M H$_2$SO$_4$. Adapted from ref. [143].

As can be seen, the data obtained for the Ir(111)-oxides in perchloric acid reveal their remarkably high OER activity among the most active extended Ir catalytic surfaces.

5.5 Rotating microelectrode

Until now the investigation of the gas evolution reaction has been performed at low over-potential, i.e. when $j_{\text{meas}} < 10$ mA cm$^{-2}$. This choice was necessary due to the formation of a non-conducting gas-phase at the interface which complicates the catalyst activity assessment at high catalytic currents, thus impeding the understanding of material properties [173–176]. In fact, a number of serious difficulties arise when trying to investigate the performance of gas-evolving catalysts under industrial reaction conditions. Among the classes of electrocatalysts in use, oxide materials are essential for numerous applications related to the catalysis of gas-evolving reactions. An important challenge with oxide catalysts is the assessment of their electrochemical properties. The first issue is that an accurate quantification of the specific activity is not straightforwardly feasible [177–179]. Methodologically, it is difficult to immobilize oxide materials at the surface in a way that the geometric area of common electrodes is reasonably close to the real electroactive surface. Notably, common methods used in classical heterogeneous catalysis, e.g. the Brunauer–Emmett–Teller (BET) method, are often not reliable in this case since there is no direct correlation between the BET-determined surface area and the
electrochemically active surface area [180]. Furthermore, errors originating from blocking of pores by adsorbed \( \text{H}_2\text{O} \) and \( \text{OH}^- \) [181] can invalidate the determination of the real area with the BET method. The removal of \( \text{H}_2\text{O} \) and \( \text{OH}^- \), even under vacuum conditions requires temperatures high enough to provoke sintering of oxides [182]. Alternatives, e.g. EIS, are often difficult to apply due to the poorly understood double layer frequency dispersion phenomenon, where multiple hardly predictable parameters can lead to unacceptable errors in the determination of the surface area based on the “interfacial capacitance” [183–186].

Another distinctive feature of gas-evolving electrodes is that the active sites at the surface are periodically or stochastically blocked by gas bubbles, complicating the assessment of intrinsic catalytic properties. The normally used “macro” (i.e. from several millimeters to several centimeters in diameter) rotating disk electrodes give unacceptably large noise due to the gas evolution process even at relatively small current densities of \( \sim 20 \text{ mA cm}^{-2} \) and even using high rotation velocities [93, 187–189]. Therefore, the comparison of oxide electrocatalysts is often performed at a current density of \( 10 \text{ mA cm}^{-2} \) [32, 34, 96, 190]. These current densities are too small to be seriously considered in real large-scale applications, which require at least one order of magnitude higher values [16, 191]. Furthermore, in the case of a partially covered and non-planar geometry, misinterpretation of data resulting from hydrodynamic experiments performed via RDE is also a common source of errors [73].

In this chapter, an approach which minimizes the influence of the most serious issues complicating the performance assessment of thin film oxide electrocatalysts for gas evolution reactions is proposed. The proposed approach consists of several steps. The first step involves the electrochemical deposition of the thinnest possible oxide film which demonstrates the highest catalytic activity on a “macro” electrode, without displaying any noticeable influence of the substrate. Roughness and porosity of the catalyst layer is consequently minimized. The oxide film is then electrodeposited on microelectrodes with a typical diameter of approximately 25 \( \mu \text{m} \), which is opening the possibility to visualize the complete electrode surface by means of atomic force microscopy (AFM). This allows a reasonable (it is assumed that the dimension of a catalytic center is not smaller than \( \sim 0.3 \text{ nm} \)) assessment of the roughness and the further comparison of the surface morphology after stability measurements. The following steps involve activity/stability measurements using the rotating microelectrode (RME) setup, which minimizes the influence of the formed gaseous product. The combination of the small surface area and the hydrodynamic method performed with RME enables gas evolution experiments at high current density.
densities relevant for industrial applications that are normally not achievable by using the standard RDEs. This approach allows further reduction of the surface blockage by gas bubbles and diminishes mass transport limitations. As model objects of the investigation, one of the state-of-the-art industrially relevant oxygen evolution reaction electrocatalysts is used, namely CoOx films.

5.5.1 CoOx film electrodeposition

CoOx thin films were chosen as model catalysts for the OER, as they are known to be active and relatively stable [192, 193]. Their key advantages are the high abundance, low costs, relatively good thermodynamic stability, and low electrical resistance [194]. It should be, however, taken into account that bubble nucleation and bubble departure are strongly correlated to the film morphology [195] which, in turn, also affects the electrocatalytic properties of the oxide. Thus, one of the goals was to minimize the catalyst surface roughness.

In order to achieve this goal, a film having the minimum thickness exhibiting bulk-like catalytic properties of the oxide was deposited. CoOx electrodeposition occurs according to the following reactions [196]:

\[
\text{Co}^{2+} + (n+2) \text{H}_2\text{O} \rightarrow \text{CoO} \cdot n \text{H}_2\text{O} + 3 \text{H}^+ + e^- \quad \text{(Equation 29)}
\]

\[
2 \text{Co}^{2+} + (n+3) \text{H}_2\text{O} \rightarrow \text{Co}_2\text{O}_3 \cdot n \text{H}_2\text{O} + 6 \text{H}^+ + 2 e^- \quad \text{(Equation 30)}
\]

The resulting Co-oxide deposit is non-stoichiometric. Accordingly, in the following paragraphs the deposited cobalt oxide film will be referred as CoOx. The solution used for the deposition process contained 0.1 M CoSO\(_4\), 0.1 M CH\(_3\)COONa, and 0.1 M Na\(_2\)SO\(_4\) (the procedure of deposition is described in ref. [197]). In order to have a more precise control over the CoOx layer thickness, electrodeposition was performed by means of cyclic voltammetry. An example of CoOx deposition is shown in Figure 52, where CoOx film formation is characterized by a pair of anodic/cathodic waves growing from cycle to cycle. The voltammetric charge involved in the Co deposition is obtained by integrating the anodic parts of the voltammograms. This charge gives, in turn, a rough estimation of the nominal film thickness.
Figure 52: Electrodeposition of CoO\textsubscript{x} on a Au-electrode in subsequently performed cyclic voltammograms (scan rate 20 mV/s). Different colors visualize the increase in anodic and cathodic current related to the oxidation/reduction of Co(II)/Co(III). Reprinted with permission from [198]. Copyright (2016) American Chemical Society

5.5.2 Oxygen evolution on “macro” electrodes

The activity of the catalyst was measured as a function of the increasing amount of CoO\textsubscript{x} deposited (see Figure 53) in order to find the charge corresponding to the thinnest possible film which demonstrates the highest activity for the OER without exhibiting any influence of the substrate. Figure 53 shows, for the case of “macro” Au-, Pt-, and GC-electrodes, that the thickness of CoO\textsubscript{x} deposited onto the electrode surface and the nature of the electrode substrate material influence the overall OER activity of the obtained catalyst deposits. After a rapid increase for small amounts of deposited CoO\textsubscript{x}, the activity stabilizes from a voltammetric charge of \( \sim 15 \text{ mC cm}^{-2} \). When the CoO\textsubscript{x} deposition charges exceed 15 mC cm\(^{-2}\), the support material does not influence the catalytic activity. Hence, it can be affirmed that in this case the catalytic activity depends solely on the properties of the CoO\textsubscript{x} film. This is a fundamental issue because the turnover frequency for the OER is influenced by the substrate for very thin Co-oxide catalyst layers, and it decreases to that of bulk CoO\textsubscript{x} as the thickness of the cobalt oxide deposit increases, as was shown in ref. [199].
Figure 53: Dependence of the OER activity ($j_{\text{OER}}$) (measured in 0.1 M KOH) of CoO$_x$ thin films deposited on Au, GC, and Pt “macro” electrodes on the charge related to the deposition of the catalyst. The charge is calculated from the electrodeposition process in Figure 52. Activities are obtained at 1.83 V vs RHE and they are not corrected for the uncompensated resistance to avoid additional sources of possible errors in determination of the minimal film thickness exhibiting the bulk-like catalytic activities. Each dot represents a unique activity measurement for a freshly deposited film. Lines are given as a guide for eyes. Reprinted with permission from [198]. Copyright (2016) American Chemical Society.

In order to morphologically characterize the films, AFM analyses were performed. In Figure 54A, an AFM image of a deposited film with a very small nominal thickness is shown, corresponding to the case when the activity is influenced by the nature of the underlying electrode material. In Figure 54B the AFM image of a relatively thick film is depicted, corresponding to the case with supposedly no influence of the underlying electrode material on the activity. The voltammetric charges corresponding to the minimum thickness exhibiting bulk-like catalytic properties were then chosen for the CoO$_x$ film deposition on the microelectrodes.
5.5.3 CoO\textsubscript{x} deposition on UME

In a similar fashion as for “macro” electrodes, the morphology of the CoO\textsubscript{x} film deposited on Pt microelectrodes has also been characterized by means of AFM as shown in Figure 55. The diameter of the microelectrodes (25 µm) enables the visualization of the whole electrode surface as well as estimation of the real roughness of the film. The precise assessment of the real roughness permits, in turn, a very rigorous determination of the specific activity for the OER by normalizing the current to the surface area, which is very close to the real one. It should be emphasized that the morphology of the electrode surface is important because bubbles are formed preferentially at certain nucleation sites. The activity of the catalyst is additionally determined by the amount and properties of these surface sites. Consequently, with the complete characterization of the surface it is in principle possible to link the observed activity changes to the morphology of the layer. Using line profiles as those shown in Figure 55, it is possible to calculate the real (electrochemically active) surface area of microelectrodes with high accuracy and ensure that the deposited film is quasi-uniform.
The observed concavity in Figure 55 is caused by the hemispherical diffusion of the reactants during the deposition process on the microelectrode. The difference in height profiles corresponds to ~2% changes as compared with the whole electrode surface, thus one-dimensional diffusion models are fully applicable in this case.

Figure 55: AFM characterization of a deposited CoO\textsubscript{x} thin film: (A) 2D image of the microelectrode surface after deposition. (B) A typical AFM line profile through the center of the microelectrode after CoO\textsubscript{x} deposition. The axes are plotted in two different scales (µm on the x-axis and nm on the y-axis) to stress the height difference in the line profile, corresponding to only ~2% changes as compared to the size of the whole electrode. Reprinted with permission from [198]. Copyright (2016) American Chemical Society.

Importantly, the ratio between the inert housing diameter and the diameter of the electroactive CoO\textsubscript{x} surface is much higher for a microelectrode than for conventional macroscopic electrodes used for RDEs experiments. This high ratio further reduces unwanted possible problems with e.g. the current density, which is effectively uniform across the entire surface of the microelectrode.

5.5.4 Activity measurements and stability assessment using the RME setup

After the morphological characterization, the electrocatalytic properties of the CoO\textsubscript{x} electrocatalyst deposited on microelectrodes were assessed under different experimental conditions in the RME setup. The overpotential for the OER is determined by the combination of activation and diffusional potentials. Therefore, the measured activity depends on both intrinsic kinetic properties of the electrocatalyst and mass transport in solution (see Equation 11). The exact calculation of the contribution of the mass transport on the overall measured current for a disk in a regime of “diffusion limited current” can be performed by using defined models. The first is the linear diffusion model, which is applicable for common RDE measurements under
mass-diffusion limitation and is described in chapter 4.2. The second is the hemispherical diffusion model and can be applied on UME disks experiments as described in chapter 4.3. As none of these regimes can be applied for the OER for reasons discussed above, the estimation of the intrinsic catalytic properties of the catalysts is challenging [189, 200].

The electrocatalytic activity in case of a “macro”-electrode is determined by the most active sites on the surface [201], where the morphology of the surface allows a faster nucleation and release of gas bubbles. Nevertheless, for the assessment of the electrocatalytic properties of the catalyst the current is normalized over the whole surface, including spots on which bubbles departure is significantly hindered due to the morphology (i.e. the surface is almost permanently blocked by the insulating gas phase). With the RME configuration proposed, the linear and hemispherical diffusion are combined, thus greatly enhancing the mass transport. Consequently, there is a faster removal of the gaseous products, which significantly reduces the blockage of the surface enabling a more precise assessment of the intrinsic activity of the catalyst. The reduction of $j_{ms}$ allows a more precise assessment of the intrinsic activity of the catalyst as well as the effect of the rotation rate on the linear sweep voltammogram (LSV). LSV measurements at quasi-static conditions in the RME configuration are thus performed to evaluate the activity of the CoO$_x$ catalyst, as depicted in Figure 56.

![Figure 56: LSV measurements performed in the RME configuration for CoO$_x$ films in O$_2$-saturated 0.1 M KOH solution at different rotation rates and without microelectrode rotations. Scan rate: 1 mV/s. Reprinted with permission from [198]. Copyright (2016) American Chemical Society.](image-url)
As mentioned in chapter 5.1, the correct determination of the uncompensated resistance is fundamental for a correct evaluation of the activity. The RME configuration solves this issue allowing almost perfect iR-drop free measurements as the measured electrode potential is close to the real one with a maximum of 1-2 mV difference (Figure 57).

Figure 57: Typical EIS (○) of a microelectrode in 0.1 M KOH. Fitting (black line (→)) was performed with the EEC represented in the inset according to the procedure described in chapter 5.1.

When the LSVs recorded at 3000 rpm are compared with the ones obtained at 1000 rpm or under “static” conditions (Figure 56) it can be seen that the hydrodynamic regime indeed remove O₂-related effects. These effects originate from the formation of the gaseous phase product and possible changes in the local pH value due to high current densities. Hence, a more accurate characterization of the catalyst film properties at industrially relevant current densities (≥~0.2 A cm⁻² [11]) becomes possible. The absence of significant mass transfer influence on the measured current allows the observation of quasi-Tafel relationships at higher current densities. This, in turn, permits a more comprehensive analysis of the electrode kinetics.

Under static conditions, a noticeable negative deviation from linearity is observed before industrially relevant current densities are reached, whereas under rotation the deviation from linearity occurs only at larger overpotentials. All polarization curves show deviations from a “Tafel line” at high current densities (see Figure 58). This can be attributed to uncompensated Ohmic resistances, but it can also reveal a change in the Tafel slope itself. The Ohmic resistance increases with higher current density due to the presence of gas bubbles in the electrolyte and upon blockage of active surface sites by bubbles, thus reducing the effective surface area. Both effects converge to an increased deviation from the actual Tafel line with increasing
overpotential. Thus, it is necessary to perform an appropriate correction for the obtained polarization curves in order to extract meaningful data for the Tafel plot analysis.

With the aim of distinguishing between Ohmic effects and changes in the Tafel slope, Equation 31 can be applied to approximate the electrode potential $E$ at each current value:

$$E = a - b \ln I + RI$$  \hspace{1cm} \text{(Equation 31)}

where $a$ and $b$ are the Tafel constant and slope, respectively, $R$ is the uncompensated resistance, and $I$ is the measured current. However, taking into account the resulting values of $R$, that are estimated using EIS, and the measured current densities, the correction of the electrode potentials is negligible in case of a microelectrode (see Figure 57). From the intercept $a$, the exchange current density and hence the standard heterogeneous rate constant of the reaction $k_0$ can be calculated. However, due to the irreversibility of OER, the principle of reversibility does not apply in this case [29]. As a consequence, the steady state kinetic data on the OER can only yield mechanistic information concerning the RDS described by the Tafel slope ($b$-coefficient). For OER, $b$ generally has a value between 30 and 120 mV dec$^{-1}$ [202], and it indicates whether the RDS is a first or a second electron transfer step, and if a chemical reaction is involved.

In Equation 31, $R$ is assumed to be a constant independent from the current. This implies that the uncompensated resistance is usually underestimated for gas evolution reactions. Consequently, the calculated $R$ deviates significantly from the correct value and leads to an incorrect estimation of the reaction kinetics. In fact, a continuous increase in the Tafel slope with applied potential may simply be the result of a reduction in the effective electrode surface area with increasing gas evolution speed. Therefore, caution should be taken when interpreting multiple Tafel regions in terms of a possible mechanistic pathway. The fitting of the quasi-linear part of the voltammogram for the determination of the Tafel slope has been performed at 3000 rpm in order to minimize the effect of the mass-transport overpotential and the uncompensated resistance caused by gas formation.
Figure 58: Logarithm of the current density $j$ as a function of the overpotential $\eta$ for the OER calculated from LSV at 1 mV/s and at a rotation speed of 3000 rpm (see Figure 56). Orange, magenta, blue, and green squares represent the relevant current densities at 0.4 A cm$^{-2}$, 0.3 A cm$^{-2}$, 0.2 A cm$^{-2}$, 0.1 A cm$^{-2}$, respectively. The linear Tafel fit of the experimental values is represented by a red line. From ref. [198].

From Figure 58, it can be seen that a linear relationship between log($j$) and the overpotential is given up to almost industrial current densities. This leads to a more reliable analysis of the OER kinetics close to application conditions. Figure 59 shows the results of galvanostatic experiments, which were then performed at 3000 rpm and at industrially relevant current densities using CoO$_x$ thin films on Pt microelectrodes and on an unmodified Pt microelectrode. At the beginning of the experiment, the difference in overpotential between CoO$_x$ and PtO$_x$ is $\sim$0.7 V at the same current density and rotation rate. The overpotential for OER on the Pt electrode increases with time due to the formation of Pt oxide on the surface [203]. CoO$_x$ exhibits an overpotential of $\sim$0.66 V at a current density 0.4 A cm$^{-2}$ and of $\sim$0.51 V at a current density of 0.17 A cm$^{-2}$, respectively.
Figure 59: Galvanostatic measurements in RME configuration in O$_2$-saturated 0.1 M KOH at 3000 rpm. Measurements were performed with CoO$_x$ microelectrodes at 0.17 A cm$^{-2}$ (red squares) and at 0.4 A cm$^{-2}$ (black squares), and with an unmodified Pt microelectrode at 0.4 A cm$^{-2}$ (blue squares). From ref. [198].

The effect of the rotation rate on the overpotential for galvanostatic experiments at a current density of 0.4 A cm$^{-2}$ on Pt and CoO$_x$ microelectrodes is shown in Figure 60. Faster rotation rates increase the diffusion of the gaseous products from the surface, thus reducing the reaction overpotential.

Figure 60: Galvanostatic measurements performed at 2000 and 3000 rpm on CoO$_x$ (black and red squares, respectively) and on Pt (pink and green squares, respectively) microelectrodes.
5.5.5 Corrosion evaluation

In Figure 61, separate galvanostatic experiments with CoO$_x$ at 0.17 A cm$^{-2}$ and 0.4 A cm$^{-2}$ at 2000 rpm are shown to demonstrate the final degradation of the catalyst on different electrodes.

Figure 61: Time dependence of the electrode potential during galvanostatic polarization at 2000 rpm at an effective current density of 0.17 A cm$^{-2}$ (black squares) and 0.4 A cm$^{-2}$ (red squares) using a CoO$_x$ thin film deposited on Pt-microelectrodes. Note that the electrode potential suddenly increases when the CoO$_x$ thin film electrocatalyst is completely removed from the surface due to degradation. The catalyst layer is removed first during the galvanostatic polarization at 0.17 A cm$^{-2}$ because this experiment has been performed after the galvanostatic polarization at 0.17 A cm$^{-2}$ at 3000 rpm for 300 s as depicted in Figure 59.

The sudden potential increase at ~160 s and ~350 s in Figure 61 at 0.4 A cm$^{-2}$ results from partial blockage of the surface by gas bubbles. At 0.17 A cm$^{-2}$, the CoO$_x$ catalyst layer was completely degraded after about 11-12 min (the same CoO$_x$ catalyst layer was used before for the galvanostatic polarization at 0.17 A cm$^{-2}$ at 3000 rpm as depicted in Figure 59). After degradation the overpotential increased until reaching the value close to that for an unmodified Pt microelectrode. The status of the catalyst after the galvanostatic experiments has been characterized by means of AFM. The 2D AFM image and the profilometry of the microelectrode, Figure 62A and B respectively, visualize the depletion of the catalyst after the galvanostatic experiments.
AFM characterization offers an alternative approach for quantification of the corrosion rate of oxide electrocatalysts with respect to techniques which are used nowadays such as inductively coupled plasma mass spectrometry [148, 172, 204, 205], quartz crystal microbalance [206, 207] and RRDE [208, 209]. The thickness of the corroded catalyst layer after voltammetric and galvanostatic experiments is 200 nm as derived from the AFM images, which corresponds to a corrosion rate at industrial current densities up to ~10 mm per year. It can be noted that the higher pH values of solutions used in industry might reduce the local pH variations at the surface during OER, thus possibly reducing the degradation rate of the material.

Many aspects of catalyst corrosion, however, remain controversial. Catalyst degradation is influenced by many parameters (cell potential, potential dynamics, temperature, pH value, impurities, etc. [209]) which hamper a standardized investigation protocol. In case of high surface area nanoparticles, several degradation mechanisms are involved such as particle detachment from the conductive support, particle agglomeration and dissolution, or Ostwald ripening. Moreover, the estimation of parameters describing a nanoparticle-based catalyst (catalyst loading, particle size, interparticle distance) is challenging. Bulk or thin films catalysts allow the morphological characterization of the electrocatalyst surface, thus avoiding the aforementioned problems occurring in the case of nanoparticles. However, when bulk or thin films catalyst are employed, the current densities used for stability quantification are one order of magnitude lower than industrially used current densities [148, 172, 207].
Nevertheless, the proposed benchmarking method prevents challenges of high-surface area catalysts and at the same time enables quantification of the corrosion rate of the catalyst at industrial current densities.

### 5.6 Chlorine / oxygen selectivity

In order to investigate the effect of the electrolyte composition on the selectivity of the CER/OER, a new set-up was developed. The effect of the anode composition on the selectivity has been intensively studied [23], but there have been comparatively few studies on the effect of additives to the electrolyte on the CER selectivity. The only experiment involving addition of non-specifically adsorbing species (as NaNO₃) resulted in an increase in the oxygen evolution rates in the chlorate process [210]. Nevertheless, industrial CER and chlorate production differ substantially in the composition of the electrolyte and in many reaction parameters, e.g. the pH value of the electrolyte in the chlorate process is adjusted between 6 and 7 [211], whereas for CER the pH value in the anode compartment is 3 [19, 21]. The rate of the CER is obtained by the Nernst equation:

$$E \left( \text{Cl}^-/\text{Cl}_2 \right) = E^0 \left( \text{Cl}^-/\text{Cl}_2 \right) + \frac{RT}{2F} \ln \left( \frac{f(\text{Cl}_2)}{\gamma(\text{Cl}^-)c(\text{Cl}^-)} \right)$$  \hspace{1cm} (Equation 32)

Where $f(\text{Cl}_2)$ is the fugacity of Cl₂, $\gamma(\text{Cl}^-)$ is the activity coefficient of Cl⁻ and $c(\text{Cl}^-)$ is the concentration of Cl⁻ in solution. The overpotential for the CER is lower as the concentration and the activity of Cl⁻ increase. On the other hand, the activity of water deviates from the value of 1 for a solution with high ionic concentration (i.e. > 0.1 M), and decreases as the concentration of salt increases [212]. When the number of water moles used to hydrate the cations and anions in solution is higher, the quantity of “free” water molecules decrease. Thus, the addition of a further salt in solution, e.g. NaNO₃, diminishes the quantity of “free” water molecules available for the parasitic OER, reducing the undesired O₂ gas produced. To prove this concept a new set-up for the CER investigation has been developed (see Figure 63).
5.6.1 Chlorine evolution setup for gas analysis

The first fundamental issue when dealing with CER regards the high corrosiveness of gaseous Cl₂. The most important consequence is that the CER reaction needs a dedicated mass spectrometer connected to the electrochemical set-up via a PEEK capillary. In fact, Cl₂ corrodes stainless steel tubes as the ones which usually connects the electrochemical reactor to the quadrupole chamber of the mass spectrometer. The high corrosiveness of gaseous Cl₂ has revealed to be in particular a problem for the shaft of the rotating unit. The long (i.e. > 4 hours) galvanostatic experiments implicate a prolonged exposure of the shaft to the Cl₂ containing atmosphere. A titanium shaft was therefore designed for the purpose of the experiments. The rotating shaft being slightly off-axis led to exposure and with this to corrosion of the stainless steel ball bearings of the rotator. The ball bearings were therefore replaced by glass-ball bearings. An electrode-holder made of PEEK was furthermore realized.

Ar was used as carrier gas at a constant flow of 100 mL/min during galvanostatic measurements. Anodic and cathodic compartments had different volumes, therefore a constant and equal overpressure in the whole reactor had to be ensured. In order to do so, the gas outputs of the two chambers were connected to a single gas release to balance the pressure. The combined gas output was directed into a concentrated 5 M KOH solution to disproportionate Cl₂ into hypochlorite and chloride [213]. The pH value of the solution varies as H₂ is evolved at the cathodic side. Therefore, an autotitrator was used to keep a constant pH value of 3 in the solution by means of the addition of 1 M HCl. The pH-sensitive electrode was placed in a separate chamber, connected with both anodic and cathodic compartments via Teflon tubes. The solution was circulated from the pH-meter compartment to the electrochemical reactor by means of a peristaltic pump. The electrolyte flow from the anodic side to the pH-meter compartment was considerable higher than the one from the cathodic compartment. This was done in order to maintain a continuous and rapid flow of the electrolyte from the cathodic to the anodic compartment and to ensure that the measured pH value reliably reflected the pH value at which Cl₂ was evolved.
CER experiments have been performed in a 4 M NaCl solution using a dimensional stable anode (DSA) as electrode. The air-tight electrochemical cell was connected to a mass-spectrometer for gas analysis. Experiments were performed under galvanostatic control at a current density of 0.4 A cm\(^{-2}\) and the proton concentration was kept constant at pH 3 by automatic titration with 1 M HCl. An example of the gas detected at the mass spectrometer during a galvanostatic CER experiment is shown in Figure 64, in which the ionization current of Cl\(_2\) detected in the mass spectrometer is plotted against the time. The constant current of 0.4 A cm\(^{-2}\) was applied for \(~2000\) s, and both the electrolyte and the cell atmosphere were saturated with Cl\(_2\) after a period of \(~1100\) s, thus a constant amount of Cl\(_2\) was detected after this saturation time. The Cl\(_2\) ionization current undergoes a rapid increase when the amplification of the Cl\(_2\) detection was increased from \(10^{-13}\) to \(10^{-12}\) A to optimize the sensitivity of the mass spectrometer.
Cl₂ evolution proceeds in parallel with the OER, thus to establish the Cl₂/O₂ selectivity, the ratio of the two gases was examined. In Figure 65 the ionization current of Cl₂ and O₂ is represented. 

Figure 64: Ionization current representing the Cl₂ detected as a function of time in a galvanostatic CER experiment. Chronoamperometric measurement performed at 0.4 A cm⁻² from 0 to ~1600 s. At ~1100 s the amplification of the QMS was changed from 10⁻¹³ to 10⁻¹² A.

Cl₂ evolution proceeds in parallel with the OER, thus to establish the Cl₂/O₂ selectivity, the ratio of the two gases was examined. In Figure 65 the ionization current of Cl₂ and O₂ is represented.

Figure 65: Ionization current detected with the mass spectrometer for O₂ and Cl₂ as a function of time. Detected gases are produced by means of a galvanostatic polarization experiment at 0.4 A cm⁻² at a pH value of 3.

At the used experimental conditions (i.e., T = 25 °C, 4 M NaCl, pH 3), the selectivity should be in the order of 97±1% for Cl₂ [195]. The Cl₂/O₂ ratio is consistently lower in the
experiments due to the insufficient vacuum of the quadrupole chamber of the mass spectrometer, i.e. $7 \times 10^{-10}$ bar instead of an optimal $1 \times 10^{-9}$-$10^{-10}$ bar range, causing a substantial increase of detected O$_2$. The background noise thus hinders a reliable analysis of the composition reaction gas and impedes further studies with the use of the mass spectrometer.

5.6.2 Selectivity study by means of RRDE

A new approach involving the use of the RRDE has been developed for the analysis of Cl$_2$/O$_2$ selectivity. The disk of the RRDE setup was used as anode for the CER reaction. Commercial IrO$_2$ nanoparticles where chosen as model catalyst for this series of experiments. IrO$_2$ has been reported to show a 100% faradaic efficiency for the OER [214], and it is expected to have the same faradaic efficiency for the CER. The dissolved Cl$_2$ generated at the disk was reduced by 2 electrons at the surrounding Pt ring electrode kept at a constant potential of 1 V vs Ag/AgCl. Figure 66 shows a plot of the collection efficiency at the ring as a function of the disk current. Note that at low collection efficiencies, the measurements are affected by a substantial deviation. In fact, small errors in the ring current can lead to relatively large errors in the determined collection efficiencies. This issue was previously noted by McCrory et al. [34] when calculating the faradaic efficiency of oxide catalysts for OER. For this reason, the analysis of the collection efficiencies was performed at higher current densities. However, at current densities $>1$ mA cm$^{-2}$, local Cl$_2$ saturation forms bubbles at the disk electrode, causing a reproducibility problem as only dissolved Cl$_2$ can be collected at the ring electrode. Furthermore, as mentioned before, for gas evolution reactions such as CER and OER it is not possible to reach the $j_{\text{limited}}$ regime via RDE measurements. Thus, the collection efficiency comparison was performed at anodic currents representing a compromise between low current densities, and high current densities at which gas bubbles are produced (see Figure 66).

Another issue concerning the RRDE approach is that the experiments to determine the selectivity were performed at non-steady state conditions. This is because the galvanostatic experiment causes an increase of dissolved Cl$_2$ in solution, thus increasing the background current at the Pt ring due to Cl$_2$ reduction.
The Cl$_2$ / Cl$^-$ reduction current becomes lower as the concentration of NaNO$_3$ increases at a constant $j_{\text{disk}}$, suggesting a decrease in selectivity towards Cl$_2$ gas evolution with an increasing ionic strength. The results seem to confirm the previous observation for the chlorate process by Jaksić et al. [210]. However, the interpretation of the selectivity results for this RRDE experiments is not straightforward, because the solution viscosity varies substantially with increasing addition of NaNO$_3$. In fact, mass transfer overpotential increases with the viscosity, i.e. with the increase of NaNO$_3$ concentration. Figure 67 represents the change in kinematic viscosities ($\nu$) for the different solution employed in the RRDE experiment.

Figure 66: Current densities at an IrO$_2$ anode plotted against the collection efficiency for the Cl$_3$/2 Cl$^-$ reaction at the Pt ring. Scan rate 50 mV/s. $E_{\text{ring}} = 1$ V vs. Ag/AgCl. pH 3, Ar-saturated solution. $j_{\text{anode}}$ is normalized to the geometrical area of the anode. IrO$_2$ loading 210 µg cm$^{-2}$. 

The Cl$_2$ / Cl$^-$ reduction current becomes lower as the concentration of NaNO$_3$ increases at a constant $j_{\text{disk}}$, suggesting a decrease in selectivity towards Cl$_2$ gas evolution with an increasing ionic strength.
Kinematic viscosity values allow for the quantitative estimation of the $j_{\text{ms}}$ for the solutions employed. Indeed, using the Koutecky-Levich equation and performing experiments at steady state regime at different $\omega$, the diffusion coefficients can be derived [215]. The selectivity can then be calculated under the same $j_{\text{ms}}$ value for all solutions employed, assuring a meaningful analysis of the selectivity results. However, for catalysts immobilized in Nafion films, the stability is an important issue. In this case the catalyst adhesion is insufficient due to the high shear forces caused by the electrode rotation in high density solutions, thus it is not possible to perform the necessary steady state measurements for the Koutecky-Levich analysis.

Furthermore, the oxide catalyst needs to be electrodeposited on the RRDE disk in order to ensure a higher stability for RRDE measurements at steady-state conditions and a reliable calculation of the diffusional term. In fact, when the catalyst nanoparticles are immobilized inside Nafion, diffusional limitations in the active Nafion/catalyst layer also play a fundamental role, and the diffusion transport of the gases inside it needs to be taken into account [216, 217].

![Figure 67: Kinematic viscosity as a function of the concentration of NaNO$_3$ in 4 M NaCl solutions employed for the selectivity measurements in Figure 66. The red dotted line represents the exponential increase trend of the obtained viscosities.](image.png)
6. Conclusions

The improvement of the performance of electrocatalysts is of great importance for many technologically significant reactions. For this purpose, great efforts are directed towards the understanding of electrochemical interfaces and the assessment of the activities of various catalytic materials. To achieve this, it is of utmost importance to avoid certain methodological and instrumental issues and take particular care of experimental conditions in the assessment and benchmarking of the activity of catalytic processes for various reactions.

It has been demonstrated how the catalyst surface structure and composition as well as electrolyte components contribute to the unique properties of an electrified interface using well-defined systems. However, lack of experimental data for various important systems complicates a complete understanding of materials properties. Model Pt(111) and Ir(111) were therefore used to extend the experimental investigations of model surfaces to assess the properties of metal/electrolyte interface.

For Ir(111) the PME was assessed in acidic solutions containing both adsorbing (sulfates) and non-adsorbing (perchlorate) anions. PMEs were estimated together with the $E_{PZTC}$, which is closely related to the work function. Knowledge about those is a key requirement for a detailed understanding of the interfacial properties of a catalyst. Ir(111) single crystal electrodes properties were analyzed in aqueous acidic solutions using LIPT, cyclic voltammetry and CO-displacement techniques. At first, voltammetric profiles of Ir(111) in solutions containing either non-adsorbing ions (perchlorate) or adsorbing ions (sulfates) were studied. CVs in perchlorate containing solutions from pH 1 to pH 5 evidenced distinctive features, in the so-called H-upd region, which changed as the proton concentration increased. On the other hand, voltammetric profiles of Ir(111) at pH 1, pH 2 and pH 3 in sulfate-containing solutions showed a shift of the sulfate adsorption peak of 30 mV per pH unit. The PME has been assessed via LIPT measurements in perchlorate containing solutions from pH 1 to pH 5 and in sulfuric acid solutions from pH 1 to pH 3. Laser transients in perchlorate containing solutions showed drastic dissimilarities as compared to Pt(111). On Ir(111) a slower hydrogen adsorption process was detected and the PME shifted 30 mV per pH unit, instead of remaining constant in the SHE scale as for the PME of Pt(111). Moreover, it appears located within the H-upd region, i.e. $E < 300$ mV vs RHE, in all the pH-dependent studies. This result evidences that hydroxyl is likely adsorbed at ~0.25 V vs RHE in perchloric acid solutions and suggests that the surface in the overall double
layer region is positively charged. CO-displacement experiments also determined the $E_{PZTC}$ in perchlorate containing solutions from pH 1 to pH 4. The values of $E_{PZTC}$ confirmed the hypothesis that the H-UPD region should not only involve hydrogen adsorption but also OH adsorption. Experimental values of $E_{PZTC}$ and PME were compared at different pH values. The potential difference between PME and $E_{PZTC}$ decreased with decreasing proton concentration in solution. Furthermore, the $E_{PZTC}$ was higher than the PME, suggesting that at the $E_{PZTC}$ the surface excess of hydrogen is higher than that of adsorbed OH. Both LIPT and CO-displacement measurements have shown the pivotal role of the specific nature of the anion (either hydroxide or sulfate) in the redistribution of the charge across the interface. Comparison of the trends of PME values of Ir(111) and Pt(111) as function of the proton concentration displays the high influence of the pH value on the interfacial properties. Their PME discrepancy vs their difference in the work function (under vacuum conditions) evidenced the fundamental solvent-induced change on local surface potentials, in particular for Ir(111). The solvent-induced change on local surface potentials consequently determines the overpotential at which the intermediates for the electrocatalytic reactions (e.g. H and OH) can adsorb onto the catalyst.

However, relatively simple relationships describing interactions between the reaction intermediates and the electrode surface are often influenced by “spectator species”, which notably complicate the interpretation of experimental data. In fact, in this work it has been shown that electrolyte components which are typically not considered to be directly involved into electrocatalytic gas-evolution processes demonstrate significant or even drastic influence on the activity, stability and selectivity of electrocatalysts.

The “spectator species” influence on oxidation processes and gas evolution reaction on model Pt(111) and Ir-oxide films grown on Ir(111) electrodes were investigated as well as the influence of nitrate anions on the CER.

Electrolyte anions such as perchlorate and sulfate have been demonstrated to influence the oxidation process of Ir(111) and the OER on AIROF. Specific adsorption of sulfate ions on Ir(111) hinders the oxidation of the metallic surface thus shifting the reaction to more positive potentials. Sulfates also decrease the AIROF activity towards OER if compared to the reaction performed in a solution containing non-specifically adsorbing perchlorate anions. For the model Pt(111), investigations on its oxidation kinetics and the place-exchange process associated with its oxidation have been conducted. The study did not achieve any unambiguous conclusion, except for the exclusion of the influence of Cl$^-$ anion on the aforementioned processes. The
influence of ClO$_4^-$ and SO$_4^{2-}$ anions on the HER and HOR on Pt(111) were furthermore analyzed, showing that they did not change the electrocatalytic activity of the catalysts. In fact, perchlorate and (bi)sulfate are not adsorbed in the relevant potential range of the reactions, and the CVs for the HOR coincide with the theoretically calculated ones using Nernst equation and assuming diffusion control. On the other hand, it was shown that alkali metal cations (Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) noticeably influence the catalytic activity of Pt(111) electrodes towards the OER, HER and HOR in sulfuric acidic media.

Sulfate anions likely make interactions between electrolyte components and reaction intermediates very complex, resulting in non-linear catalytic trends from Li$^+$ to Cs$^+$ containing electrolytes. While there have been indications that for some processes (such as the (bi)sulfate adsorption) it is possible to describe those interactions with simple descriptors such as, for instance, the hydration energy, observations of the catalytic activity of model electrodes in acidic media largely suggest that the situation is more complex. Nonetheless, the effect of the non-covalent interaction between cations and sulfates on tuning the activity of the Pt has to be considered in the design of electrocatalytic systems with improved performance. Among the tested electrolytes, the ones containing Rb$^+$ demonstrated a noticeable and systematic influence, increasing the activity of the Pt(111) electrodes towards the model electrocatalytic processes studied. While it is difficult to clearly elucidate the origin of this effect, this empirical finding can likely be used as an interesting point to further explore the impact of the electrolyte components on electrocatalysis.

The effect of the electrolyte composition on the CER performed on a DSA electrode was also investigated in this work, focusing on the selectivity between the two gases, O$_2$ and Cl$_2$, evolved in the process. NaNO$_3$ has been chosen as the “spectator” component of the electrolyte. It has the role of being the ionic source that reduces the number of “free” water molecules available for the parasitic OER. For this purpose, a new set-up connected to a QMS has been developed, but insights on the selectivity were not obtained due to the low vacuum of the mass spectrometer quadrupole chamber, which hindered reliable analysis of the gas evolved. A new approach to investigate the selectivity has been attempted by the use of a RRDE. The approach consists on CER at the catalyst on the disk (namely IrO$_2$ nanoparticles immobilized in a Nafion film) and the reduction of the gaseous products at the Pt ring. Data obtained suggest an increase of activity for the parasitic OER with higher NaNO$_3$ concentration, but further analysis regarding the influence of the solutions viscosity on the results needs to be performed.
The issues encountered during the investigation about the selectivity in the CER underline how an insufficiently precise assessment of the effect of “spectator anions” can mislead the evaluation of reaction kinetics and overpotentials. In fact, it is important to ensure that the differences between experimental results are due to differences in electrocatalytic activity and not caused by methodological issues.

The importance of experimental conditions in the assessment and benchmarking of the activity of catalytic processes for various reactions is necessary to address these issues and implement widely accepted protocols that will improve reproducibility and permit more meaningful evaluation of results. Particularly, experimental aspects regarding the correction of the uncompensated ohmic resistance using impedance spectroscopy measurements were analyzed. Issues regarding the uncompensated resistance are especially relevant for gas evolution reactions, where a non-conducting gas phase is accumulated in the system, hence influencing the activity measurement.

Furthermore, for the scope of addressing experimental issues and implementing the current assessment of activity of catalytic processes generating gaseous products, a relatively simple approach was developed. The methodology is based on benefits provided by the use of microelectrodes, and it evaluates accurately the performance of oxide electrocatalysts for gas-evolution reactions at high current densities, relevant for industrial application. The approach involves electrochemical deposition of the thinnest possible oxide films which demonstrate the highest, bulk-like catalytic activity, without displaying an influence of the underlying electrode material. The model catalyst chosen was CoO$_x$, which is among the state-of-the-art materials for OER in alkaline electrolyte. Films of CoO$_x$ were deposited on microelectrodes that simultaneously solve two issues. It is possible to visualize the whole electrode surface with AFM for a detailed assessment of the surface roughness, and to minimize the influence of the formed non-conducting gaseous products. The combination of the small surface area and hydrodynamic conditions caused by the high rotation speed allows reaching high current densities. The values reached via RME method consented the characterization of the catalyst at industrially relevant current densities which are normally not achievable by using the standard state-of-the-art protocols. The proposed relatively simple methodology permits an exhaustive evaluation of the catalyst activity and stability at virtually any current density from industrial relevance.

To summarize, this work provides new insights into the electrolyte/catalyst interface, which is necessary for a predictive basis to design and optimize catalysts, especially taking into
account the high cost of Ir and Pt. The influence of the electrolyte components on gas evolving electrocatalytic reactions was brought into consideration and their influence on catalyst activities was analyzed. Furthermore, a new methodology for the characterization and evaluation of the catalysts has been proposed, which is a much needed aspect in the field of electrocatalysis.

7. Experimental

7.1 Uncompensated resistance

Working electrolytes were prepared using 96% H₂SO₄ (Merck, Suprapur), 70% HClO₄ (Merck, Suprapur) and 0.1 M KOH solution (99.99 %, Sigma–Aldrich). For the OER experiments, a thin layer of cobalt oxide was deposited on an FTO (NSG TEC 8 A, Pilkington) surface. For this, a solution was prepared using Na₂SO₄•10 H₂O (≥ 99%, AppliChem, and ≥ 99% Sigma-Aldrich), CH₃COONa (≥ 99%, J.T. Baker, and ≥ 99% Sigma-Aldrich), and CoSO₄•7 H₂O (≥ 99%, Sigma Aldrich). The film was deposited by 50 voltammetric cycles in a potential range between 0.51 V and 0.54 V vs. MMS reference electrode.

The experiments were performed using a Bio-Logic SP-300 potentiostat. The algorithms used to fit the data from EIS spectra has been reported previously [218]. CV experiments were performed using a scan rate of 50 mV/s in argon-saturated (Ar 5.0, Air Liquide), oxygen-saturated (O₂ 5.0, Air Liquide) and hydrogen-saturated (H₂ 6.0, Air Liquide) solutions. The probing frequencies in EIS experiments were varied between 30 kHz and 100 Hz with a 5 mV amplitude of the probing ac signals. Before the beginning of each experiment using Pt(111) single crystals, the quality of the surface was assessed with characteristic cyclic voltammograms.

7.2 HER and OER experiments on Pt(111) and on AIROF

The electrochemical cell used for the HER and OER experiments on single crystals is described in detail elsewhere [219]. Before the experiments performed with Pt(111), all glassware was cleaned with 0.01 M HF followed by subsequent multiple rinsing with ultrapure water. HER and OER experiments were performed using Pt(111) and Ir(111) single crystals, respectively, with a sample diameter of 5 mm, surface roughness of 30 nm, and orientation that is better than 0.1° (Mateck, Germany). The preparation and characterization under of the single crystal hanging meniscus configuration before each experiment of Pt(111) was described in detail in ref. [220].
A Hg–HgSO₄ electrode and a Pt wire (GoodFellow) were used as reference and counter electrodes, respectively. Working electrolytes were prepared using H₂SO₄ (Merck, Suprapur), Na₂SO₄ (99.99% Sigma Aldrich), K₂SO₄ (99.99% Sigma Aldrich), Li₂SO₄ (99.99% Sigma Aldrich), Cs₂SO₄ (99.99% Sigma Aldrich) and Rb₂SO₄ (99.98% Sigma Aldrich). The Pt(111) and Ir(111) electrodes were always immersed in the electrolytes under potential control at 0.05 V vs. RHE. In Figure 68 a scheme of the preparation procedure for OER and HER experiments and an AFM image of the Ir(111) surface prior the AIROF growth are shown.

Figure 68: (A) Schematic representation of Pt(111) and AIROF for HER and OER experiments. (B) AFM image of the Ir(111) surface prior the AIROF growth proving the quality of the crystal surface. From ref. [143].

The OER experiments on AIROF and Pt(111) were performed in an oxygen-saturated solution (O₂, Air Liquid, Germany) at 800 rpm. Prior to each OER experiment on AIROF the surface was always freshly prepared starting from the Ir(111) followed by the oxidation of the surface in an anodic scan. AIROF were grown via potential cycling between 1.575 V and 0.7 V vs RHE until stable CVs were obtained. This procedure produces stable voltammograms for the OER in O₂-saturated electrolytes. The HER and HOR experiments on Pt(111) were performed in hydrogen-saturated solutions (H₂ 6.0, Air Liquide, Germany) at 1600 rpm. EIS measurements were performed with probing frequencies in the range between 30 kHz and 100 Hz with 10 mV amplitude of the probing signals. Before the beginning of each experiment with Ir(111) and Pt(111), including the OER measurements, the quality of the single crystal surface was assessed.
with characteristic cyclic voltammograms. The experiments were performed using a Bio-Logic SP-300 potentiostat.

7.3 Oxidation of Pt(111), LIPT and CO-displacement experiments on Ir(111)

Before each LIPT and CO-displacement experiment, the Ir(111) electrode was annealed by means of inductive heating in a Ar (Ar 5.0, Air Liquide, Germany) + H₂ (6.0, Air Liquide, Germany) atmosphere. Annealing and cooling were performed under a flow of Ar + H₂ in a ratio of 3:1, and the crystal was heated at a temperature higher than 1600ºC for 300 s. The energy was provided by an induction coil and its power supply (Hu 2000, Himmelwerk, Germany); the annealing temperature was checked by a pyrometer (IGA 140, Impac Infrared, Germany). The quartz tube was partially filled with ultra-clean water in equilibrium with the H₂/Ar gas mixture and the Ir(111) was transferred to the working cell protected with a drop of this water.

Perchloric acid electrolytes were prepared using HClO₄ (Merck 70%, Suprapur, Germany), KClO₄ (monohydrate, 99.99% Merck, Germany), and NaF (99.999%, Merck, Germany). The sulphate/sulphuric acid solutions were prepared using respectively K₂SO₄ (99.999%, Merck, Germany), and H₂SO₄ (Suprapur 96%, Merck, Germany). In all solutions ultrapure water (18.2 MΩ cm) obtained from an Elgastat water purification system was used. The pH values of the different solutions were measured using a pH-basic-20 pH-meter from Crison coupled with a pH-probe pH 50 12 HACH model.

To perform the LIPT measurements a four-electrode cell was employed. Two Pt wires were used as a second working electrode and as a counter electrode, respectively. As a reference electrode a Pd wire was employed, previously charged with H₂ in a different compartment. The potentials recorded with the Pd/H₂ reference electrode shifted by +50 mV with respect to the RHE electrode and were then converted to the RHE scale. All experiments were performed with the Ir(111) in the hanging meniscus configuration.

The procedure for recording the laser transients was described in detail elsewhere [120]. To summarize, before recording the laser transient, cyclic voltammetry was recorded using a µ-Autolab III potentiostat (Metrohm-Autolab, Utrecht) using the current integration mode, to check for the cleanliness and stability of the surface. A second auxiliary electrode made of Pt was used as an internal reference to measure the potential transient. At the beginning of each experiment, both working and second auxiliary electrode were polarized at the same potential. Approximately 200 μs before firing the laser both electrodes were disconnected from the potentiostat. The
potential difference between both electrodes was measured at open circuit. As the laser pulse only affects the single crystal working electrode, the measured potential difference is related to the response of the Ir(111)/aqueous solution interface. Each experiment was repeated with a frequency of 10 Hz to ensure that the temperature relaxes to the initial value between measurements. The potentiostat was reconnected between successive laser pulses to keep the potential at the desired value. In this way 128 or 256 potential transients were recorded and averaged using a Tektronix Model TDS 3054B oscilloscope. Finally, after recording all potential transients, the cleanliness of the interphase was checked by recording a voltammetric profile.

The duration of the pulse was 5 ns and the laser used had a having a d=6 mm and was a 532 nm frequency (double harmonic) Nd-YAG (Brilliant B from Quantel). A conventional arrangement of mirrors directed the laser beam to the Ir(111)/aqueous solution interface. The cell was kept into a Faraday cage to avoid electrical noise during measurements. The energy density of the laser beam was reduced to 1 mJ cm\(^{-2}\) by combining the effect of an attenuator from Newport Corporation (Model M-935-10) and the regulation of the Q-switch time. The laser energy was measured with a pyroelectric sensor head (Model M-935-10).

The procedure to perform CO-displacement measures is described in detail in ref. [87]. For this procedure, a three-electrode cell with six inlets was employed. One inlet was used for the Pt wire counter electrode, a second one for the RHE electrode contained in a lugging capillary, and a third one for the Ir(111) working electrode in the meniscus configuration. The fourth and five inlets were used for Ar bubbling and to keep control of the inner Ar atmosphere, respectively, thus preventing any flow of oxygen inside the cell that could disturb the measurement. The last inlet was for the supply of the CO gas through a glass pipeline with the outlet closely pointing the Ir(111) solution contact meniscus. Before each CO measurement, the working electrode potential was held constant at the desirable value and then a CO stream was allowed to flow. While the CO stream was dosed a transient current was recorded until the whole Ir(111) surface was covered by a monolayer of CO. Then the excess of CO in solution was removed by bubbling Ar during 10 min and the CO monolayer was stripped off electrochemically. For both, cyclic voltammograms and amperometric measurements, a waveform generator (EG&G PARC 175) together with a potentiostat (eDAQ EA161) and a digital recorder (eDAQ ED401) were employed.
7.4 RME methodology

Polycrystalline Au-electrodes (3 mm in diameter, CH Instruments), polycrystalline Pt-electrodes polished down to 30 nm roughness (5 mm in diameter, Mateck), glassy carbon (GC) electrodes (5 mm in diameter, Pine Instruments), and Pt microelectrodes were used. The procedures for the preparation of microelectrodes (diameter 25 µm) have been described in detail in [221].

The potential was controlled using a VSP-300 potentiostat (Bio-Logic) in all experiments. A Hg/HgSO$_4$ electrode (SE Analytics or Schott) and a Pt wire (Goodfellow) were used as reference and counter electrodes, respectively.

Prior to the CoO$_x$ film deposition, Au-electrodes were cycled in the potential range from 0.25 to 1.85 V vs. RHE in Ar-saturated (Ar 5.0, Air Liquide) 0.05 M H$_2$SO$_4$ solution (96% H$_2$SO$_4$ Merck, Suprapur). Pt microelectrodes, Pt “macro” electrodes, and GC-electrodes were cycled in 0.5 M H$_2$SO$_4$ from 0.05 to 1.4 V vs. RHE until reproducible voltammograms were obtained.

The working electrolytes were prepared from KOH (≥99% Merck and 85% Grüssing) by dilution with ultrapure water from Evoqua Ultra Clear 10 TWF 30 UV (Evoqua) or Siemens ultrapure (Siemens) water purification systems. Cobalt oxide films were deposited from a solution prepared using Na$_2$SO$_4$•10 H$_2$O (≥99%, AppliChem, and ≥99% Sigma-Aldrich), CH$_3$COONa (≥99%, J.T. Baker, and ≥99% Sigma-Aldrich), and CoSO$_4$•7 H$_2$O (≥99%, Sigma Aldrich) via cyclic voltammetry by cycling the potential between 1.05 to 1.55 V vs. RHE. The OER activities of CoO$_x$ films deposited on “macro” electrodes have been assessed by determining the activity as a function of the charge associated with the redox transformations in the deposited film at 1.83 V vs RHE in a 0.1 M KOH solution at a 50 mV/s sweep rate (without iR-correction).

The OER activities of the CoO$_x$ films deposited on the microelectrodes were measured in oxygen-saturated (O$_2$, 5.0, Air Liquide) 0.1 M KOH solutions at rotation speeds of 0, 1000 and 3000 rpm and at a potential scan rate of 1 mV/s. Electrochemical deposition experiments were performed in a conventional 2-compartment cell with a three-electrode setup and in a single-compartment three-electrode cell. Activity measurements were performed in a special 2-compartment 3-electrode cell in order to permit the use of RME. The RME setup is shown in Figure 69.
AFM experiments were performed in the tapping mode using a “Nanowizard 3” (JPK Instruments) and a multimode EC-STM/AFM instrument (Veeco) with a Nanoscope IIID controller.

7.5 Oxygen / chlorine selectivity

Working electrolytes were prepared using NaCl (>99.5%, Sigma–Aldrich), NaNO₃ (>99%, Roth). For all electrochemical experiments a glassy carbon (GC) RRDE-type electrode was used (4 mm diameter). Electrodes were polished to a mirror finish with a diamond slurry (3 µm) and alumina slurry (1 µm and 0.3 µm) before each measurement. IrO₂ (99.9%, Sigma–Aldrich) was immersed in a sonication bath for 10 min in order to separate particle aggregates and to obtain homogeneous powders for preparing catalyst inks. Electrochemical characterization was performed using thin-film type electrodes. IrO₂ catalyst inks was prepared using Nafion as the binder (Nafion 117 ≈ 5% in alcohol mixture). The inks were prepared to a concentration of
5 mg mL\(^{-1}\) catalyst, with the solvent containing ultrapure water (49 % volume ratio), ethanol (49 % volume ratio), and Nafion (2 % volume ratio). For preparing the catalyst layer, the ink of each sample (8.4 µL) was drop-cast on the surface of the GC electrode and left to dry in air. All solutions were saturated with Ar for 30 min and the CER experiments were performed under an Ar blanket at 50 mV/s. For all experiments a PGSTAT302N potentiostat/galvanostat (Metrohm Autolab) was employed. For the viscosimetry measurements, a Rheostress RS 75 (Haake) was used and the dynamic viscosity was measured at 31°C. for all solutions. The solutions density was measured with a density meter DMA (Anton Paar). Gas analyses were carried out using a Gam 400 (Balzers).
8. References

[21] C. Gerrath, Recent developments in chlorine processing, Zurich, Switzerland.


