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The electrode-electrolyte interface in CO2 reduction and H2 evolution: a multiscale approach

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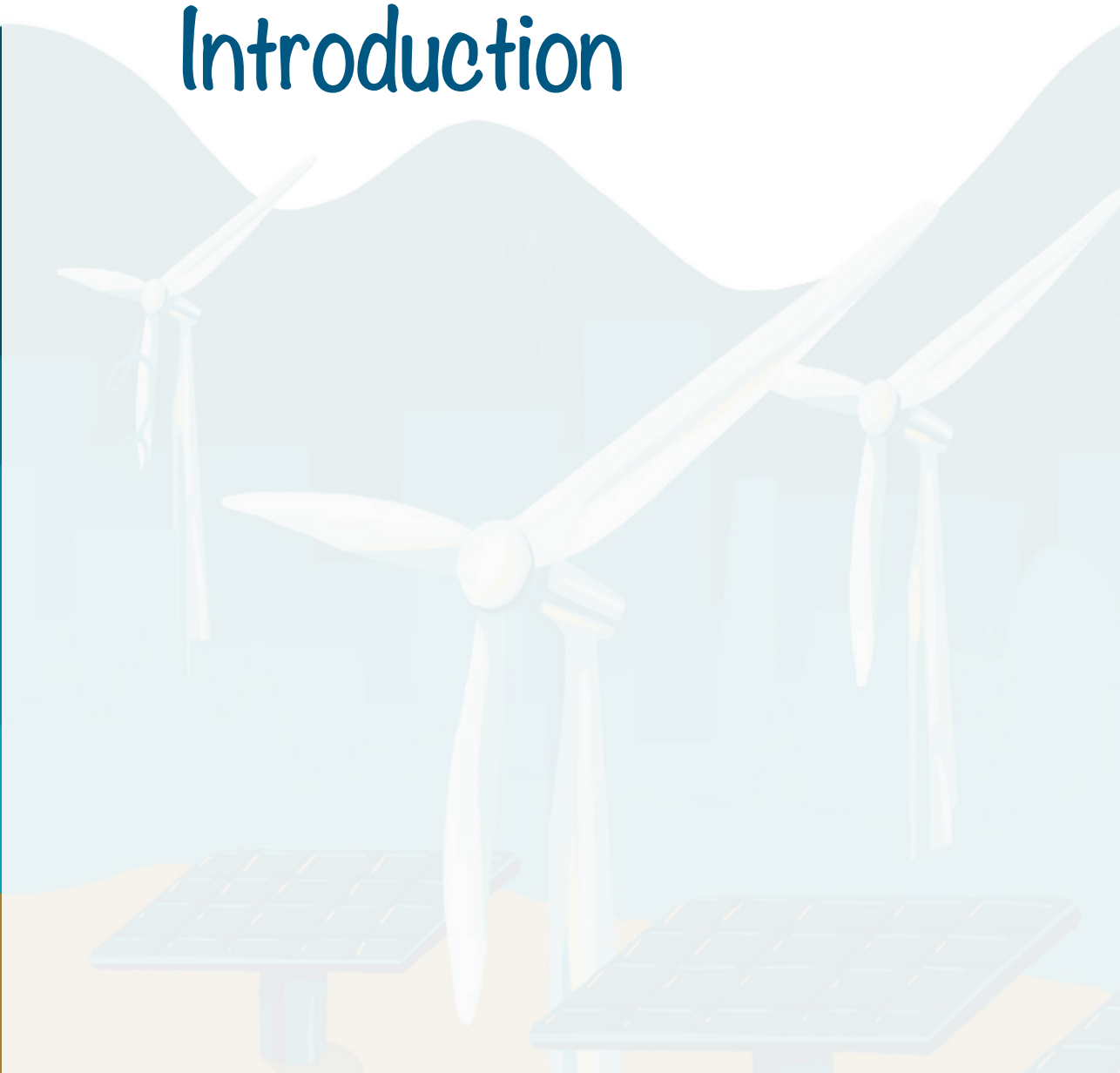
Introduction



1.1 Electrochemistry and electrification

The study of the transformation of electrical energy into chemical bonds and, in the reverse process, the conversion of energy stored in chemical bonds back to electricity, defines the field of electrochemistry. While in chemical reactions electrons are transferred directly between molecules, in electrochemical reactions they are transferred through electronic or ionic media. Electrochemistry is an old science, its birth being considered to be in the 18th century, the time of the great findings of "animal electricity" by Galvani and the first battery by Volta.[1] Various devices and processes involving electrochemistry that are currently used at an industrial scale come from concepts that were developed in the 19th century. These include batteries[2] , solar cells[3], and the industrial production of chlorine from brine.[4] The field has been increasingly growing, especially since the beginning of the 21st century, due to climate change and the need for electrification, renewable energy conversion and storage technologies. The importance electrochemistry has had and will have for the future of our society is highlighted by the 2019 Nobel Prize in Chemistry, awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino for their contributions to the development of the rechargeable lithium-ion battery in the 1970s. The battery enabled the development of mobile phones, laptops, electric vehicles and the storage of energy generated by solar and wind power. Nevertheless, further developments in electrochemistry will still be crucial for improving the current landscape of sustainable energy production and utilization, towards a fossil fuel-free electrified society.

In the last one-and-a-half century, we have relied almost exclusively on non-renewable resources to produce things that are essential to maintain our lifestyle, such as energy, chemicals, and fuels. For example, the chemical industry is highly dependent on petroleum, both as a feedstock and energy source. In fact, roughly 6-7% of the annual oil production is consumed by this sector.[5] The combustion of these fossil resources generates greenhouse gas emissions that damage our environment and lead to climate change. To remediate that, there is growing interest in using renewable energy and sustainably produced chemicals to feed the industry and transportation sectors, as these are the main consumers of fossil resources nowadays.[6] Using clean electricity as the main source of energy is a potentially cheap and efficient way to decarbonise our economy. The costs of renewables and storage technologies are rapidly falling, making it possible to achieve the required expansion of clean power systems at low cost. Overall, with

the current existing technologies (and those under development), the replacement of greenhouse gas emitting processes and the electrification of our society can be achieved by:

- Increasing the renewable energy electricity production, supply and storage capacity;
- Replacing combustion engines by electric motors, present e.g. in battery and fuel cell powered vehicles;
- Using electricity to drive industrial processes.

A very important example of a decarbonized energy system is the use of H_2 as energy storage, fuel, and bulk chemical. Renewable electricity can be converted to H_2 through the electrolysis of water. It is cheaper to transport hydrogen than to transport electricity, which means that, for example, electrolysers can be placed on sites where the renewable electricity is cheap and delivered where it is needed, on demand. The energy stored in H_2 can in turn be used when there are shortages, or H_2 can be directly used as fuel e.g. in micro combined heat and power (CHP) fuel cells in our homes, without a carbon footprint. Although electrification is already happening in the ground transportation and electricity sectors, for some industries such as cement and steelmaking this is not yet the case, and may be more challenging to achieve. Nevertheless, there are still ways of reducing the carbon footprint of these processes using electrochemistry. For instance, renewable electricity can be used to electrochemically convert CO_2, a waste from the cement and steel industries, to a chemical building block, like CO.[7] This pure CO can, for example, be used in the industrial preparation of acetic and acrylic acid, among many other applications.[8]

Achieving global electrification will require serious breakthroughs in the different industrial sectors and, importantly, in the society. A change in mentality is necessary, to drive the initial investments that relying on electricity will require. Infrastructure will be necessary, for integrating the power grid. All this will have to come with new laws and regulations, not only regarding the electricity market but also the environment. To succeed, these have to be allied to public acceptance, and political resolve. Although promising, this may be especially challenging to achieve in developing countries, facing e.g., social inequalities. Finally, climate change and the realization that we need to shift towards more sustainable processes, calls for innovation and for re-thinking industrial approaches. In view of that, to develop new electrochemical technologies and to stop depending on non-renewable resources, bridging fundamental and applied electrochemistry, is necessary.

1.2 Heterogeneous electrocatalysis

Heterogeneous electrocatalysis is the branch of electrochemistry that studies reactions occurring at the surface of an electrode, which contains or is the catalyst. Catalysts (or electrocatalysts) are materials that enable and/or accelerate a chemical reaction, by lowering the overall potential energy landscape so that the reaction barrier decreases. Electrocatalysis uses electricity to convert molecules as for example H_2O, N_2 and CO_2 into energy carriers or important building blocks for the chemical and fuel industries as CO, H_2, ethanol, NH_3. The device that makes this electrochemical conversion possible is also known as an electrolyser (Fig. 1.1), where a direct electric current drives otherwise nonspontaneous chemical reactions. In the cathode material, electrons are provided to the reactants while at the anode material electrons enter the circuit. Fig. 1.1 exemplifies an electrolyser in which the electrocatalytic reduction of CO_2 takes place at the cathode (CO_2 reduction reaction, CO_2RR, Eq. 1.1); and the oxidation of H_2O to O_2 (Oxygen Evolution Reaction, OER, Eq. 1.2) happens at the anode. The anode and cathode are placed in an electrically conducting medium containing cations and anions, called the electrolyte. Current is passed through the electrolyte due to the movement of positively charged ions (cations) towards the cathode, and negatively charged ions (anions) towards the anode. The cathode and anode may be separated by a membrane, a material that selectively allows species to go from one electrolyte compartment to another. For instance, the membrane from Fig. 1.1, selectively allows protons to move from the anode to the cathode compartment. This may be used to avoid secondary reactions or to easily separate the products made at the two different electrodes.

$$\text{CO}_2\text{RR:}\quad x\text{CO}_2 + n\text{H}_2\text{O} + n\text{e}^- \rightarrow \textit{product} + y\text{OH}^- \qquad \text{Eq. 1.1}$$

$$\text{OER:}\quad 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \qquad \text{Eq. 1.2}$$

The minimum energy input (voltage) required to drive reactions 1.1 and 1.2 (E^o_{CELL}) is the difference between the half-cell equilibrium potentials ($E^o_{CATHODE} - E^o_{ANODE}$) described by $E^o_{CELL} = -\Delta G^o/nF$, where ΔG^o is the Gibbs free energy of the overall cell reaction at 1 atm and 298 K, n is the number of moles of electrons transferred in the half-cell reaction, and F is Faraday constant (96 485 C mol^{-1}). The theoretical value of the cell potential can be calculated using the Nernst equation:

$$E_{CELL} = E^o_{CELL} - (RT/zF)\ln(Q_R) \qquad \text{Eq. 1.3}$$

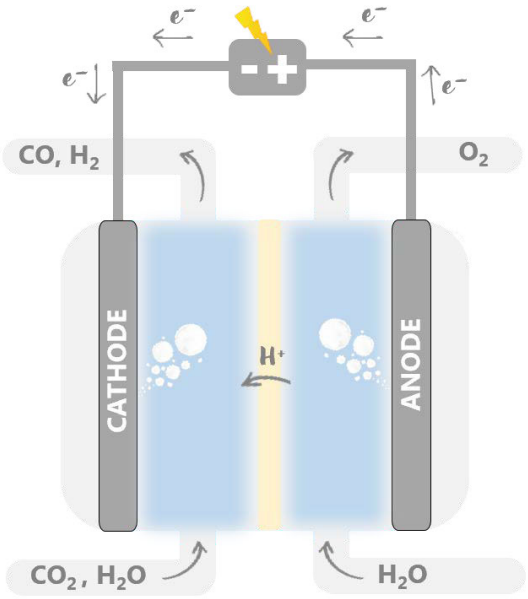


Fig. 1.1. Pictorial representation of a CO_2 to CO electrolyser, in which the cathode and anode are separated by a proton exchange membrane.

where E^o_{CELL} is the standard equilibrium cell potential, R is the universal gas constant (8.314462 J K^{-1} mol^{-1}), T is the temperature in Kelvins, z is the number of electrons transferred in the cell reaction, F is the Faraday constant and Q_R is the reaction quotient, derived from the activities of the electroactive species.

To drive sufficiently large reaction rates, an excess voltage (overpotential) must be applied to overcome the sum of several energy barriers and resistances. These include e.g. ohmic losses from the conduction of ions in the electrolyte, and the sometimes slow rates of the reactions at the cathode and anode. Studies in electrochemistry focus on minimizing the potential that must be applied for an electrocatalytic process to take place, which depends on electrode material, reactants, products, the electrode–electrolyte interface, among others. Thus, the main aim of electrocatalysis is usually to improve the reaction rate (the amount of product produced per unit of time), which can be achieved by decreasing the energy barrier of the target reaction.

1.3 The electrochemical interface

The primary role of the electrolyte is to conduct ionic charge between the electrodes. It usually consists of a solvent and a salt, that easily dissociates into cations and anions to provide a high ionic conductivity. When a metal electrode is in contact with the electrolyte, ions in the electrolyte assemble near the surface to balance the charges on the electrode. For instance, during CO_2RR, the electrode is negatively charged. Cations in the electrolyte then migrate towards the cathode surface, forming what we call the electrochemical double layer. Fig. 1.2 shows a schematic representation of the electrode-electrolyte interface according to the Gouy-Chapman-Stern theory. In this model, the double layer is composed by the Inner Helmholtz Plane (IHP), containing less solvated species and adsorbates, and the Outer Helmholtz Plane (OHP), containing fully solvated cations, which together form the Stern layer. Beyond the OHP, there are concentration gradients of the species in solution, in the region called the Gouy-Chapman diffuse layer. The charge distribution of ions as a function of distance from the metal surface, leads to a steep decrease of the electric potential extending from the electrode surface towards the bulk of the solution. The properties and composition of the electrical double layer are a function of the applied potential, the concentration and nature of the species in solution, the electrode material and reactions taking place, and can highly influence the electrocatalytic reaction.

There are different aspects of the electrode-electrolyte interface to be considered for electrocatalysis, various of which will be discussed throughout this thesis. For instance, as water participates in diverse electrochemical reactions, it is important to understand how water interacts with the surface and with the dissolved ions. Also, the degree of hydration of a cation, may dictate its concentration at the OHP, how it interacts with reaction intermediates and how it accumulates at the interface. Another important point is the dependence of the activity and selectivity of reactions on the electrolyte bulk pH. Because of that, pH gradients that may develop during a reaction that produces/consumes protons or OH^- also must be considered. All these different aspects, even though only briefly mentioned here, illustrate the complexity of the electrochemical interface. Decoupling the effects that the different electrolyte properties have on a reaction, is key towards optimizing the process and understanding underlying reaction mechanisms.

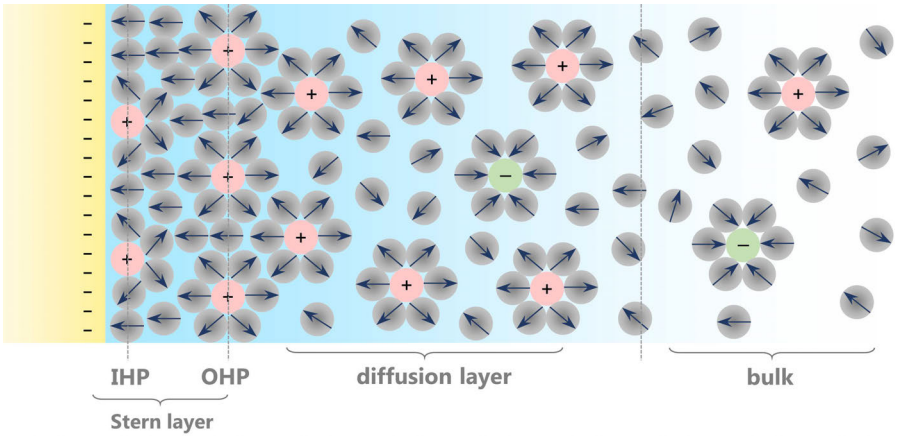


Fig. 1.2. Schematic representation of the electrode-electrolyte interface. Gray circles represent water molecules, and the arrows point towards the positive part of the dipole. Cations are represented in red and anions in green.

1.4 CO_2 electroreduction

1.4.1 Closing the carbon cycle

The first reports of the electrochemical reduction of CO_2 come from the 19th century[9], and investigations have been intensified after the pioneering works from Hori, Murata and co-workers in the 1980s.[10–12] But why to reduce CO_2? The answer is simple: because it is an abundant carbon source, processing it electrochemically does not harm the environment, and may help lowering the carbon footprint of processes. We need carbon-containing species to make fuels, chemicals, consumables, and currently we obtain this carbon mainly from processes involving fossil resources. The burning of these fossil resources produces a lot of CO_2, which is currently released into the atmosphere and contributes to climate change. In 2020, the global emissions of CO_2 reached 31.5 Gt, compared to values below 3 Gt/year before 1900.[13] Two thirds of the emitted CO_2 come from the energy sector, and the rest comes from agriculture, land use, and industries. The main goal is, of course, to stop relying on processes that emit CO_2, through electrification of the industry. Still, in cases where this is inevitable in the short term, the electrochemical CO_2RR is a way to reduce the carbon footprint of a process. In the future, CO_2RR may also help in storing excess renewable electricity in valuable products.

If instead of releasing it into the atmosphere, CO_2 is captured and utilized, it may provide the means to close the carbon cycle. Of course, at long-term, considering we will use less fossil resources and have less CO_2 waste from the energy sector, CO_2 would likely have to come from biomass processing or harvested from air, to achieve climate benefits. Also, CO_2-derived products that have a long lifetime (as building materials), offer larger emission reduction possibilities than products that ultimately involve the release of CO_2 into the atmosphere (as fuels). These, and other considerations, are of course required to access the applicability of CO_2 electroreduction, and are important for achieving a "circular economy"; a popular term nowadays which represents the idea that (carbon) waste is transformed into a fuel or building block. Such a cycle involving CO_2RR is exemplified in the schematics of Fig. 1.3. Ideally, energy from the sun and wind is converted into electricity, which powers a CO_2 electrolyser as the one showed in Fig. 1.1. The products from CO_2RR can serve as building blocks for the chemical and fuel industries, which in turn, currently emit CO_2. The CO_2 emissions can be captured and used as input to the electrolyser, leading to a net zero-emissions carbon cycle.

1.4.2 CO_2 reduction to CO

On gold, silver and zinc electrodes, CO_2RR yields mainly carbon monoxide (CO), while on Sn, Pb, Tl, Hg, In, and Cd mainly HCOOH (formic acid) is formed.[15] On copper, hydrocarbons and alcohols can be formed, such as ethylene and ethanol.[16] In this thesis, we focus on CO_2 reduction to CO on gold electrodes, as a model reaction to understand processes taking place at the electrode-electrolyte interface. The standard equilibrium potential to form most CO_2RR products, is similar to that to form H_2 from hydronium or water in aqueous electrolytes.[17] Therefore, the electrochemical reduction of CO_2 to CO (Eq. 1.4) usually competes with the hydrogen evolution reaction (HER). In acidic media, proton reduction is the main branch of HER taking place (Eq. 1.5), while in neutral to alkaline media water reduction prevails (Eq. 1.6).

$$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- \quad \text{Eq. 1.4}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{Eq. 1.5}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{Eq. 1.6}$$

Most fundamental research focuses on developing new catalysts to improve the reaction activity, selectivity and stability. Only recently, more attention has been given to optimizing the electrolyte composition[19], and to better understanding its

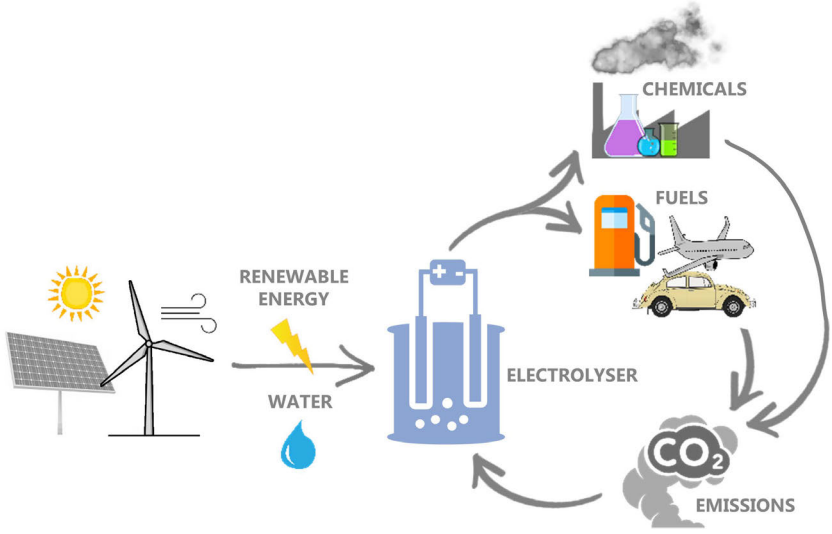


Fig. 1.3. Schematic showing the electrochemical conversion of water and CO_2 to value-added products for the chemicals and fuels industries, using energy from renewable sources. CO_2 captured from the emissions of these industries, enters the process again, closing the carbon cycle.

actual role on the reaction, which is also the focus of this thesis. Water is the most common solvent used, as it is easy to handle, safe, chemically stable, and compatible with most systems. Additionally, water can act both as proton donor and acceptor to facilitate the electrochemical reactions. Early studies on the effect of different anions and cations on the CO_2 reduction reaction, already showed that the species in the electrolyte are not mere spectators and can significantly steer the reaction activity and selectivity.[18] To date, the most reported electrolytes for CO_2 reduction are aqueous solutions of potassium bicarbonate ($KHCO_3$), due to their high buffer capacity and low price. Acidic media have usually been avoided, due to the fast kinetics of the competing proton reduction reaction (Eq. 1.4). However, we will show in this thesis that it can also be employed for efficiently running CO_2 reduction to CO. Even though CO_2 electrocatalysis is still a growing field, right now, electrolysers for the conversion of CO_2 to CO, for example, are reaching the pilot scale and are on the route towards commercialization.[20–22] This means that in the coming years, research efforts will continue to grow towards optimizing CO_2 electrolysers, and making the process more competitive.

If successfully employed at large scale, electrochemical CO_2 conversion and storage technologies have the potential to, for example, enable the sustainable production of chemicals on demand. Traditionally, CO is produced in large,

centralized plants, though e.g., gasification of coal or steam reforming. The transportation of the CO produced is expensive, as it must be pressurised and is a hazardous chemical. As of now, producing CO electrochemically at comparable scales is more expensive than e.g., via steam reforming. However, alternatively, producing CO in small decentralized electrochemical plants could allow for CO to be produced on site, according to the need. This would cut the costs of transportation and storage, make the process more competitive and improve safety.

1.5 H_2 evolution

Understanding the competing HER is relevant for improving the selectivity of the CO_2 reduction reaction. However, on its own, HER is extremely important, as the cathode reaction taking place in water electrolysers. As discussed in Section 1.1, hydrogen produced from renewable energy *via* electrolysis, has a crucial role in the global energy transition, as a clean, storable and transportable fuel.[23] There are currently three main types of low-temperature processes to make H_2 electrochemically, including alkaline electrolysis (AE), proton exchange membrane (PEM) electrolysis and anion exchange membrane (AEM) electrolysis (also known as alkaline PEM).[24] Low-temperature electrolysers are available on the market, in fact, AE have already been used for over 100 years, and account for most of the installed capacity worldwide. PEM electrolysers have been commercialized since the beginning of the 21st century, while AEM electrolysers have only recently appeared on the market. Still, the fundamental material and electrolyte properties that determine catalytic activity for the HER are not yet fully understood.[25] Fundamental research is still required in order to increase the efficiency of the electrolyser system as a whole, along with its operating life, power density and stack size, with the eventual goal of reducing costs. Mechanistic aspects of HER and further details are discussed in Chapters 9 and 10.

1.6 Multiscale approach

Throughout this thesis, we study both the fundamental and more applied aspects of electrocatalysis, or a combination thereof. On the fundamental side, electrode processes at the meso scale are mainly studied through stationary and rotating disc voltammetry. In this case, a defined portion of the working electrode area is put in contact with the electrolyte, and the current response as a function of potential is recorded. In stationary experiments, electrode reactions may face

mass transport limitations. Rotation is then used to minimize that and better control the flux of species from or towards the electrode. Going to the micro scale, investigations are carried out *in situ*, under *operando* conditions, using Scanning Electrochemical Microscopy (SECM); and *ex situ* using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDX). In SECM, a microelectrode is positioned a few micrometres in the proximity of a second electrode, where for instance a reaction is taking place. This microelectrode is used to monitor a variety of electrochemical signals, which in this thesis comprised of the local pH and the presence of H_2 and CO in the diffusion layer. SEM and EDX are techniques used before and after the electrochemical measurements, in which a focused electron beam interacts with the sample, allowing for assessing the topography and composition of the surface. At the nano scale, the electrode-electrolyte interface is modelled in this thesis using *Ab Initio* Molecular Dynamics (AIMD) and Density Functional Theory (DFT) through collaborations with ICIQ, the Institute of Chemical Research of Catalonia. We specifically look at the interaction of cations with the electrode surface, water molecules and reaction intermediates. On the more applied side, at the macro scale, we investigate CO_2 electrolysis using 10 cm^2 gas diffusion electrodes (GDEs). These are porous structures, that allow for CO_2 to be fed on one side of the structure, and the electrolyte on the other. All the reactants meet at the catalytic sites embedded in this porous structure, overcoming mass transport limitations that one would have using conventional flat electrodes. Finally, experiments involving the different scales are also conducted, combining for instance SECM and GDEs, in order to elucidate questions that one technique alone cannot answer.

1.7 Outline of this thesis

The main goal of this thesis is to study different aspects of processes taking place at the electrode-electrolyte interface and their consequences on the electrocatalysis of CO_2 reduction and H_2 evolution. **Chapter 2** provides an overview of methods available to measure the local pH during electrochemical processes, and highlights SECM as a powerful and versatile technique. **Chapter 3** describes the development of a new voltammetric pH sensor, that allows for measurements with high time resolution, high sensitivity, and selectivity. This is demonstrated by measuring the local pH during HER *in situ*, under *operando* conditions, using SECM. The sensor developed in Chapter 3, is used in **Chapter 4** to study the homogeneous reactions taking place in the diffusion layer during

CO_2RR, also using SECM. In **Chapter 5**, we combine measurements made with two different SECM probes, namely the voltammetric pH sensor from Chapter 3 and a Pt ultramicroelectrode, to understand the voltammetry of CO oxidation. We find a correlation between voltammetric features and the local pH, which arise from the reaction being limited by different species diffusing towards the surface. In **Chapter 6**, we carry out local pH measurements during HER under well-defined mass transport conditions. This is done by using a Rotating Ring-Disc electrode (RRDE) in which the ring is functionalized with the pH sensor from Chapter 3.

In **Chapter 7**, the effect of contamination of gold electrodes due to polishing is investigated. We show that Al^{3+} cations released from contaminating alumina polishing particles at the gold surface promote H_2O reduction. In **Chapter 8**, we elucidate the role of cations on CO_2RR using cyclic voltammetry and SECM. We show that this reaction does not take place on gold, copper and silver electrodes without a metal cation in the electrolyte. In combination with DFT and AIMD, the results explain the activity trends for CO formation as a function of alkali cation species, and allow proposing a new mechanism for CO_2RR. In **Chapter 9**, we broaden this study and investigate the effect of multivalent cations on CO_2RR and HER. Here, we describe how cation properties such as acidity and hydration energy determine the activity for the two competing reactions at low and high overpotentials. In **Chapter 10**, we look into the nature of differences in cation trends for HER on platinum and gold electrodes. On platinum, weakly hydrated cations inhibit HER in alkaline media, while on gold these species can either promote or hinder the reaction, depending on their local concentration at the reaction interface.

In **Chapter 11**, we scale up the experiments from Chapter 8, and investigate the feasibility of performing CO_2RR to CO in acidic media at more industrially relevant conditions. Using 10 cm^2 gold GDEs with different loadings, we show that up to 90% selectivity for CO can be achieved at high operating currents, and that running the reaction in acidic media leads to a 30% improvement in the energy efficiency. However, here, we cannot draw clear trends regarding the catalyst loading. Therefore, in **Chapter 12**, we use SECM to probe the effect of catalyst loading and CO_2 pressure on the local activity of gold GDEs. We find a slight increase in activity going from low to high loading, but that most CO produced comes from local hot spots, where CO_2 can easily access the catalyst particles. These hot spots are more abundant at high CO_2 pressures, given that there are enough catalyst particles accessible to form the 3-phase reaction boundary.

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