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Platinum surface instabilities and their impact in electrochemistry

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1 Introduction

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1.1 Electrochemistry for the Future

The global issue of climate change presents an imminent threat to the ecological balance of our planet. The rising concentrations of greenhouse gases, such as CO₂ and N₂O, contribute to increasing temperatures and extreme weather events. In addition, the world-wide growth in population urges to meet energy requirements that increase daily, thereby reinforcing the emissions of greenhouse gases. Addressing this energy and environmental crisis necessitates to transition from fossil fuels to renewable energy sources, such as solar power and wind, that can be converted into electricity. The latter can then be either used *in-situ* or stored in alternative energy forms like chemical bonds. This can be achieved by using electrochemical devices such as batteries [1], electrolyzers, and fuel cells [2,3].

Figure 1.1 represents a scheme of the operational principle of a hydrogen fuel cell, which converts the chemical energy of hydrogen into electricity [4]. In summary, hydrogen gas is supplied at the anode, where it oxidizes resulting in protons and electrons, known as the Hydrogen Oxidation Reaction (HOR) (equation 1.1). These electrons then travel through the external circuit before reaching the other electrode, the cathode. There, they combine with protons and molecular oxygen to produce water and heat, referred to as the Oxygen Reduction Reaction (ORR) (equation 1.2). The Proton Exchange Membrane (PEM) separating the two compartments acts as a selective barrier that allows only protons to pass through, while it blocks electrons and other species in solution.



The overall reaction 1.3 is a combination of the half-cell reactions taking place at the anode and at the cathode, and it delivers ideally a potential of 1.23 V, if one would neglect any power loss during the process. The power reduction stems from three main sources: the ohmic ($I R$) drop due to material and electrolyte resistances, the limitations on the supply

and transport of the reactants and, especially, the large activation barrier for the ORR [4]. This activation barrier can be reduced by using a *catalyst* as the cathode material, which provides a more optimal reaction pathway, in which the reaction intermediates bind the reaction sites neither too weakly (thereby allowing fast adsorption) nor too strongly (hence they can leave the sites promptly post-reaction) [5]. This not only boosts the reaction rate but it is also crucial to ensure that only water, and not another species such as hydrogen peroxide, is the final product [6].

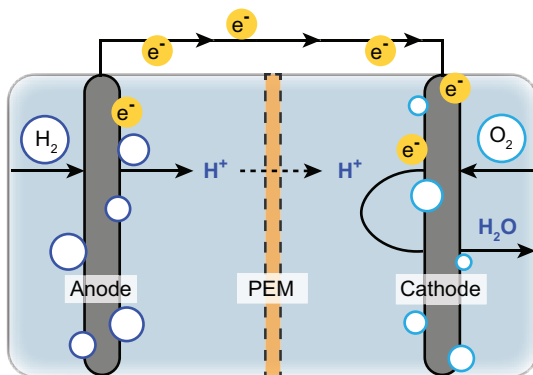


Figure 1.1: Hydrogen Fuel Cell. Scheme of a Proton Exchange Membrane (PEM) Fuel Cell that reacts H_2 with O_2 to generate electricity, with water as a product. The PEM membrane allows the transport of H^+ through, which is transported from the anode to the cathode, where it reacts.

For both the ORR and the HOR, the best catalysts known are platinum-based. However, even with these catalysts the ORR at the cathode still suffers a significant energy loss. Moreover, platinum is scarce and expensive, which hinders the industrial scalability of fuel cells using this material [3, 4]. Furthermore, it is well-known that platinum degrades and dissolves in the electrolyte upon fuel cell operation, which leads to a decrease of its electrochemical activity and ultimately to the need to replace the catalyst [7]. Therefore, electrochemical research is needed in order to optimize the platinum catalyst design, to increase its activity and stability by forming alloys, or to simply find a more affordable, abundant material that satisfies the catalytic requirements.

In addition to hydrogen fuel cells and batteries, electrochemistry could also provide an answer to convert many of the most polluting chemical processes into cleaner alternatives. The steam methane reforming process, in which hot steam and natural gas react to produce hydrogen, but also the polluting carbon monoxide and carbon dioxide as side-products, could be replaced by water splitting via electrolysis. This method generates hydrogen and oxygen gases through the reverse reaction conducted in fuel cells [3, 6]. The production of ammonia, traditionally carried out in the Haber-Bosch process by reacting nitrogen and hydrogen gases at high temperature and pressure, could also be achieved by the electrocatalytic reduction of nitrate [8]. Finally, carbon dioxide can be captured from the air and electrochemically converted into valuable fuels and organic chemicals such as methane, ethylene, and formic acid [9]. However, at present the industrial scalability of

these *green* processes is severely limited by unresolved technological challenges, as well as the economical barrier of not offering a cheaper alternative. Finding optimal electrocatalysts and reaction conditions is key for their success.

1.2 Design of an Electrochemical Experiment

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An electrochemical experiment can have different goals, from testing a particular electrocatalyst (or reaction condition) for the conversion into the desired product(s), to identifying each of the individual reaction steps, especially the one that hinders the overall reaction (the so-called rate-determining step) [10]. In any case, a typical experimental design aims to isolate the electrochemical process under study (e.g. the ORR on platinum in acidic media), which takes place at the working electrode. A second electrode, a counter, closes the electrical circuit by providing a current of equal magnitude but opposite sign to that at the working electrode. Therefore, an oxidation reaction at the working electrode will always occur simultaneously with a reduction reaction at the counter electrode, and vice-versa, although the process taking place at the counter electrode is generally disregarded. Finally, a reference electrode is used that reliably measures the electrochemical potential in the electrolyte, against which the electrochemical potential at the working electrode can be compared. This three-electrode configuration in an electrochemical (glass) cell filled with electrolyte is usually sufficient for conducting standard measurements.

The most common electrochemical experiment is cyclic voltammetry, in which the potential of the working electrode is swept through the potential range of interest before the direction of scan is reversed, simultaneously recording the current response. This technique provides a large amount of valuable information, as each of the peaks observed in the current versus potential curve represents a different electrochemical fingerprint. Therefore, by carefully studying the position, magnitude, and shape of the peaks it is possible to extract thermodynamic and kinetic parameters from the underlying electrochemical processes, which facilitates their identification [11].

1.3 Structure-Activity Relationships

In heterogeneous electrocatalysis, which is the focus of this thesis, the reactions occur at the electrode-electrolyte interface. Therefore, it is not surprising that the nanoscale surface structure of the electrode plays a crucial role on the catalytic activity [12]. This effect has been extensively studied for electrochemical reactions such as the ORR and the HOR on platinum, due to their importance in hydrogen fuel cells [13, 14]. The origin of the surface sensitivity relies on the dependence of the reaction rate with the binding strength of the reaction intermediates [15], which is closely related to the nature and geometry of the adsorption site. Thereby, surface sites with distinct coordination, such as terrace and step sites, present unlike catalytic activity [16]. Designing better catalysts requires therefore a deep comprehension of the relationship between the surface structure and the surface reactivity.

The best way to expand this knowledge is by studying the electrochemistry of single-crystalline samples. As the surface structure of these electrodes is *a priori* well-defined, a systematic study allows identification of the most active sites. Figure 1.2 shows examples of platinum surfaces with different structures, which are obtained by cutting (and polishing) a single-crystalline platinum sample with a certain orientation respect to its unit cell (the smallest repetitive unit). In order to classify the surfaces according to their orientation, we refer to a notation called Miller indexes, represented in between brackets [17]. Fig. 1.2a shows the (111) surface of a metal with a face-centered cubic (fcc) crystalline structure. This surface has the most densely packed atomic arrangement, consisting of an hexagonal unit cell, and displays adsorption sites with different coordination than the ones at the (110) surface (Fig. 1.2b) or at the (100) surface (Fig. 1.2c), which have rectangular and square unit cells, respectively. The (111), (100), and (110) surfaces are considered basal planes, as cutting the single crystal in any other orientation results in vicinal surfaces with atomic steps.

As illustrated in Fig. 1.2, the steps on vicinal surfaces can exhibit different microfacets. For example, on Pt(111)-vicinal surfaces the steps can form either a rectangular (110) microfacet or a square (100) microfacet with the lower step edge atoms, while the steps on (100)-vicinals can only exhibit a rectangular (110) geometry. Evidently, each of these atomic arrangements presents a unique local potential energy landscape and thus different electrochemistry.

Single crystal surfaces have been traditionally used in (vacuum) surface science to study material properties, surface processes, and adsorption of gas molecules, among others [18]. Typically, their preparation for surface studies involves several weeks of ion bombardment followed by electron-beam annealing in vacuum. However, the development of the flame-annealing procedure provided a relatively easier alternative to prepare single-crystalline surfaces, which boosted significantly their application for fundamental electrochemistry [19,20]. This facilitated to study relationships between surface structure and electrocatalytic activity, which enabled the identification of the most active surface sites for the ORR on platinum, among many other reactions [16]. Moreover, single crystal electrodes are also used to investigate the effect of the electrolyte or electrochemical reactions on metal surfaces, which is key to understand the fundamentals of catalyst degradation [21]. *In-situ* and *operando* characterization techniques, such as Electrochemical Scanning Tunneling Microscopy, are ideal for this purpose.

1.4 Electrochemical Scanning Tunneling Microscopy

Inspired by the development of the topografiner by Young et al. [22], in 1981 Binnig and Rohrer invented the Scanning Tunneling Microscope (STM), which represented a major leap forward in the atomic-level characterization of metal surfaces [23]. This instrument operates by scanning a sharp metal tip at a very close distance (i.e. typically less than 1 nm) from the (conducting) sample surface. When a bias voltage is applied between tip and sample in tunneling range, electrons flow between them, leading to a current that is then measured [24]. Subsequently, the tunneling current, I_t , is amplified by the pre-amp (see

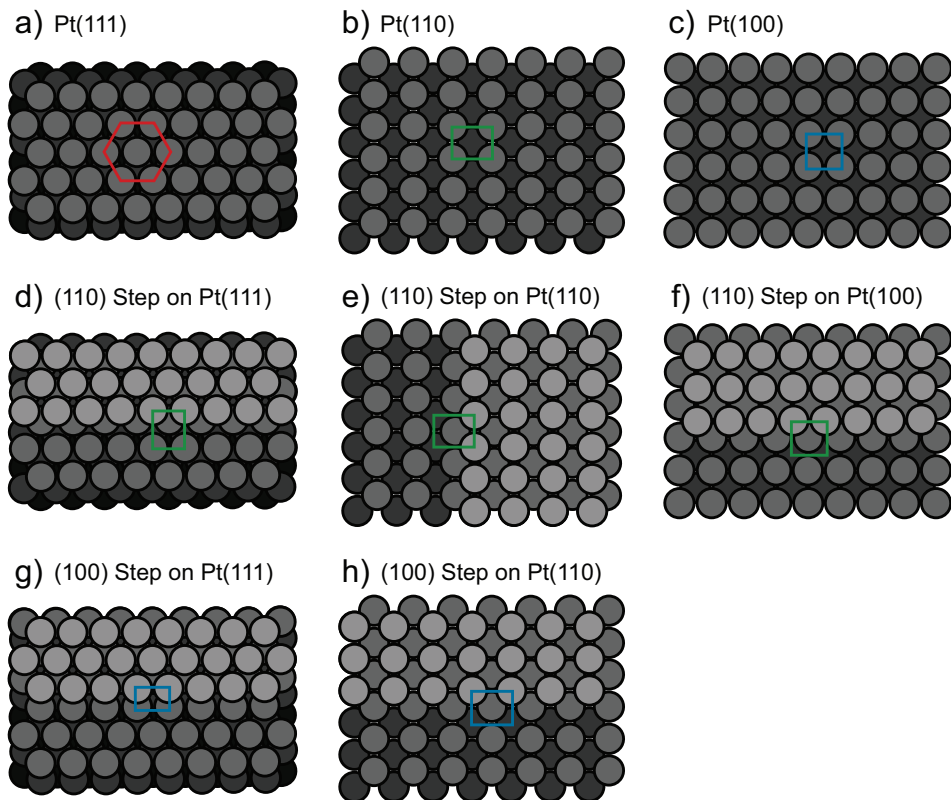


Figure 1.2: Model Single-Crystalline Platinum Electrodes. (a-c) Basal surface planes: Pt(111), Pt(110), and Pt(100), respectively. (d-f) (110) steps (also referred to as (111) steps in electrochemistry literature) on each of the basal planes, as indicated. (g) and (h) (100) steps on Pt(111) and Pt(110), respectively. The unit cells on each basal plane and the microfacets formed at the steps are indicated.

Fig. 1.3a) and turned into voltage, which exponential dependence with the tip-sample distance is linearized by a logarithmic amplifier [25]. The output signal is then compared with the set tunneling current that is applied as a target voltage. The difference between them is processed by the feedback electronics, which allows to modify the signal by applying a proportional gain (independent of the signal frequency), an integral gain (frequency dependent), and a low-pass filter, which attenuates the signals with a frequency higher than the cutoff value. Finally, the output is amplified by the high-voltage amplifiers and delivered to the Z electrode of the piezo tube, which moves the tip in height correspondingly.

A typical STM has two possible operational modes. By maintaining a constant I_t , the tip follows the surface contour, producing detailed topographic images. Alternatively, one can keep the tip height constant, and then the topographic images are generated from the fluctuating I_t . This operational mode often results in images that show atomic resolution and it

also allows for scans at higher speed, although it is severely limited to (almost) atomically-flat surfaces. Moreover, it requires a calibration in Z as well as knowing the value of the work function. In order to circumvent these issues our microscope can operate, in addition, in hybrid mode, in which the tip height is measured together with its error signal, therefore combining the benefits from both constant-current and constant-height modes [25, 26].

Only a few years after its invention, STM technology was applied also to obtain atomic-scale topographic images of surfaces submerged in liquids, giving birth to the Electrochemical Scanning Tunneling Microscope (EC-STM) [27]. The major difference between both techniques resides in the fact that, while in an STM the voltage difference is directly applied between tip and sample, in an EC-STM both tip and sample have their own voltage with respect to a reference electrode potential that is measured in the electrolyte. This was achieved by incorporating a bipotentiostat [28–30], which allowed for the direct characterization of the surface under electrochemical conditions. However this leads to experimental complications, as it requires the stability of three feedback loops working with each other: one for the tip potential, another for the sample potential, and a last one for the tunneling current I_t .

The work function (Φ) for a metal submerged in electrolyte is remarkably lower than the one in vacuum. I_t depends exponentially on both Φ as well as on the distance between the tip and the sample ($d_{tip-sample}$) [25]:

$$I_t \propto \exp(-1.025 \sqrt{\Phi} d_{tip-sample}) \quad (1.4)$$

Therefore, in electrolyte one needs to tunnel with an I_t orders of magnitude larger in order to scan the tip at the same $d_{tip-sample}$ than in vacuum. Scanning further away from the surface results in a decrease of the imaging resolution, as the geometric integral of the tunneling current coming from the surface picks up more undesired current from the sides than directly from under the tip. Moreover, in electrochemical conditions both tip and sample are exposed to any reactions that might take place, which lead to faradaic currents at the tip that directly couple to the tunneling current, thereby interfering with the imaging. In order to minimize this problem, the STM tip is usually coated with an insulator material leaving only the very apex exposed.

Figure 1.3b shows a schematic representation of the EC-STM cell together with the bipotentiostat. The sample is placed on a sample holder that allows tuning of its height with nm accuracy. A quartz cell is placed above the sample, with a viton o-ring in between that seals the connection. Clamps on the sides of the cell hold it together, preventing any leakage. The cell is filled with the working electrolyte, which flows in and out with the help of a peristaltic pump. The counter electrode is a Pt wire, while the reference electrode is a Reversible Hydrogen Electrode connected to the counter and working electrodes, tip and sample, via thin tubing. The STM-tip is made from a PtIr wire and is isolated with a polymer coating. Finally, all electrodes are connected to a bipotentiostat, which sets the desired tip and sample voltages with respect to the reference electrode potential.

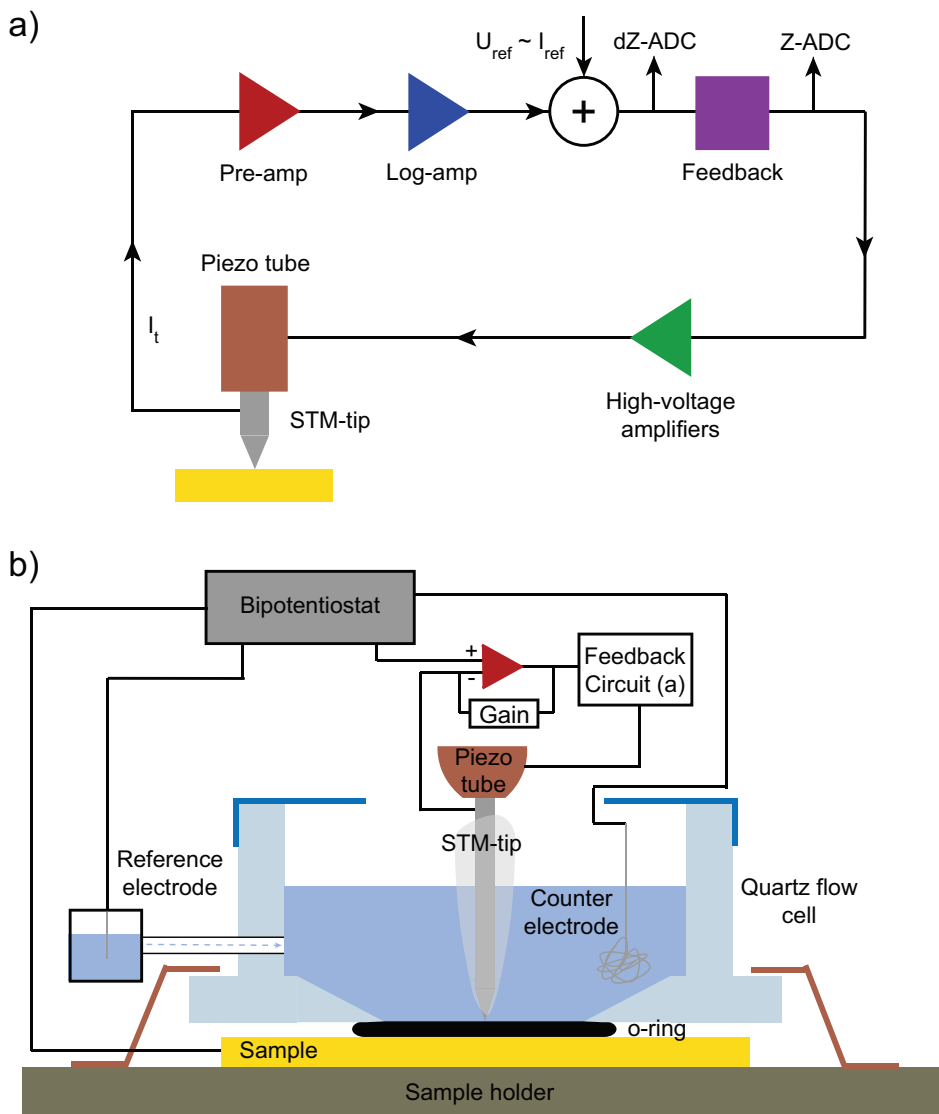


Figure 1.3: Feedback circuit of an STM and scheme of an EC-STM cell. (a) The tunneling current measured at the tip (I_t) is amplified and turned into a voltage by the pre-amp before its exponential dependence with the tip-sample distance is linearized by the log-amp. The signal is then compared with a chosen current setpoint, which is applied as a target voltage. The resulting error (dZ) is treated by the feedback and amplified by the high-voltage amplifiers, before it is delivered to the Z electrodes of the piezo tube, which move the tip in height correspondingly. The tip height (Z) is given by the output voltage of the feedback. Both the Z and dZ signals are converted into digital via their respective ADCs (Analog to Digital Converters) before being processed by the computer. (b) The sample and cell are clamped down onto a sample holder. The electrolyte flows in and out of the cell with the help of a peristaltic pump. I_t is measured at the tip, while the electrochemical current is measured at the sample. The sample and tip voltages are measured with respect to the reference electrode potential by using a bipotentiostat.

1.5 Outline of this Thesis

This thesis presents a study on the (in)stability of single-crystalline platinum electrodes in an electrochemical environment and how the surface structure changes affect the electrochemistry. *In-situ* characterization with EC-STM allows us to establish structure-activity relationships that are crucial for the development of more efficient catalysts. In Chapter 2, we study the nucleation and growth of adatom islands on a Pt(111) surface upon oxidation-reduction cycling. With the help from Density Functional Theory, we provide both a thermodynamic and a kinetic explanation to why the islands form during the reduction of the surface oxide, although the adatoms are formed during the oxidation. Moreover, we provide EC-STM evidence that the adatom islands have a dendritic shape as well as an explanation of the growth instability that leads to the formation of the dendritic branches.

In Chapter 3 we show with EC-STM that stepped platinum surfaces with high step density undergo step bunching, which is an instability that results in terraces wider than the nominal value and steps with multiple atomic-layers height. This new insight challenges the common assumption in electrochemistry that all stepped surfaces present a regular array of monoatomic-height steps. Knowing this, we prove quantitatively that this structural effect is responsible for many anomalous step density-dependent trends reported in the literature, such as the ones linking the step density to the ORR activity and the potential of zero total charge.

In Chapter 4 we expand the existing knowledge regarding the electrochemical adsorption of hydrogen and oxygen on stepped platinum surfaces. Our quantitative results show that, on all surfaces studied, the voltammetric peak related to hydrogen desorption from the steps involves more than the simple desorption of one hydrogen atom per unit step length. On the other hand, at high electrode potentials, the adsorption of oxygen leads to the formation of PtO₂ along the steps. Finally, we link this chapter to the previous one by showing that less hydrogen and less oxygen adsorb at step bunches compared to single steps.

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