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Evolution of Au(111) electrode surface in different electrolytes and conditions studied with a home-made EC-STM
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Chapter 1

Introduction

This chapter provides an overview of the theoretical foundation underlying the experimental techniques utilized in this thesis. Section 1.1 outlines the fundamental concepts and methods in electrochemistry.

1.1 Electrochemistry

The roots of electrochemistry trace back to the late 18th century through the experiments conducted by Volta and Galvani[1], marking the initial connection between chemistry and electricity. Over time, the definition and range of electrochemical science have undergone changes[2], and since the 1980s, the field of electrochemistry has experienced significant evolution. Many electrochemical (EC) experiments are conducted at the interface between distinct chemical phases, commonly involving an electronic conductor (the electrode) and an ionic conductor (the electrolyte). Typically, the electrode is a metal, and the electrolyte is a liquid solution containing a salt, acid, or base in water. At this interface, the characteristics of the two adjacent phases diverge significantly from those of the bulk. The process at this interface holds central importance and varies with the electric potential drop across it. In the case of excess charge on the metal surface, the ions with opposite charges on the solution side of the interface will compensate for this charge by creating the corresponding excess of cations or anions. Such a structure acts as a capacitor. Since the charge carrier concentration in the electrolyte is always lower than in a metal, the charge in the electrolyte expands diffusely (3 to 20 Å) into the solution. This charge distribution in a very narrow space is known as electrical double layer (EDL) and stands as a

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fundamental concern in the field of electrochemistry. As is shown in Figure 1.1a, the EDL can be made up of several layers and the layer closest to the electrode surface is called the inner layer, which contains solvent molecules and ions or cations that are specifically adsorbed[3]. They make the inner Helmholtz plane (IHP) at a distance x_1 from the electrode. Solvated ions can approach the metal to a distance x_2 and their interaction with the electrode is only electrostatic, so it is independent of the ions type and the chemical properties of the electrode. They are called nonspecifically adsorbed and form the so-called outer Helmholtz plane (OHP).

Beyond the outer Helmholtz plane (OHP), the diffuse layer extends into the solution bulk. Within this three-dimensional space, nonspecifically adsorbed ions are distributed by a combination of electrostatic interactions and thermal motion. The thickness of the diffuse layer depends on several parameters, primarily the ionic strength of the solution and the electrode potential. The potential profile in the double layer is illustrated in Figure 1.1, denoted by a solid line for nonspecifically adsorbed anions and a dotted line for the specifically adsorbed ions [4]. In the case of nonspecifically adsorbed ions, the potential varies from the metal surface to the outer Helmholtz plane (OHP) linearly like a capacitor. But it does not drop linearly to the solution potential φ_s , as in the diffuse layer it drops off exponentially from φ_2 to φ_s . In the other case, since more charge is accumulated on the electrode surface than the required charge by electrostatics, the potential overshoot to φ_1 is lower than the bulk potential. To be able to compensate for this extra charge, the countercharge will be brought into the double layer.

1.1.1 The electrochemical cell

In the experiment, measuring an isolated interface is not feasible, and at least two electrodes separated by one (or more) electrolyte phases are required. This represents the most basic form of what is commonly known as an electrochemical (EC) cell. Within an electrochemical (EC) cell, an electrical current can be generated by a chemical reaction (Galvanic cell) or, conversely, an electrical current can drive a chemical reaction (electrolytic cell). The total reaction within an EC cell is typically divided into two half-reactions: reduction occurring at the cathode and oxidation taking place at the anode. Unlike redox reactions in solution, in the electrochemical (EC) experiments, oxidation and reduction take place at different locations, where the exchange of electrons specifically accrues on the electrodes. In the majority of electrochemical (EC) experiments in a research laboratory, a three-electrode cell is used, consisting of

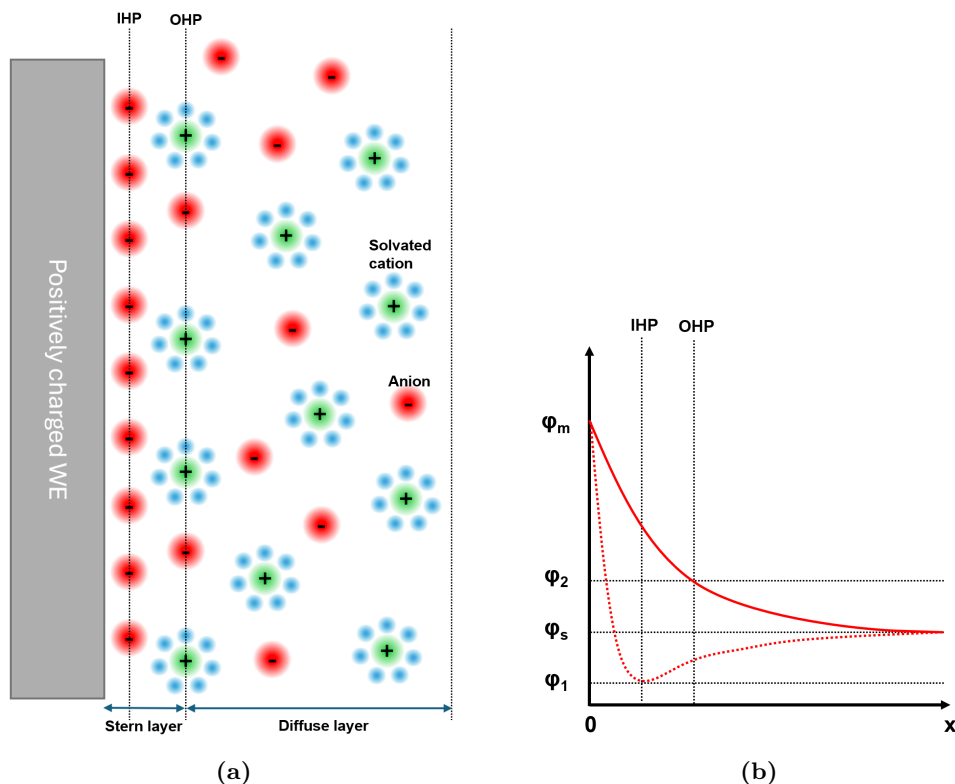


Figure 1.1: a) The model for the double layer region which contains the inner Helmholtz plane and the outer Helmholtz plane. b) Potential distribution near the electrode for non-specifically adsorbed anions as a solid line and specifically adsorbed anions as dotted line.

a working electrode (WE), reference electrode (RE), and counter electrode (CE). The working electrode (WE) is where the processes or reactions under study occur. Due to the movement of ions between the working electrode (WE) and counter electrode (CE), an electrical current flows through the cell and the potential of the working electrode (WE) is measured with respect to the reference electrode (RE). In other words, one can consider the reference electrode as a virtual ground for the electronics, so all the voltage differences can become meaningful for electrochemistry. Additionally, having just two electrodes (WE and CE) would entail the contribution of CE/electrolyte interface and electrolyte characteristics like resistivity on the applied potential on the working electrode. By adding the third electrode, we can exclude the CE/electrolyte interface contribution to the experiment and minimize the electrolyte resistance effects on the reactions under study. The potential of the reference electrode should

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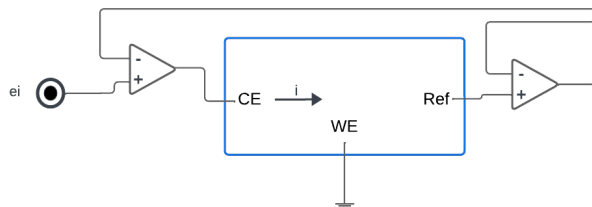


Figure 1.2: A very simple schematic of a potentiostat with three connections to the EC cell.

be well-defined, so there are many different types of reference electrodes for various experimental setups. Moreover, the reference electrode should not contribute to the current flowing in the EC cell. Thus the current on the reference electrode should be zero in the ideal case, but in practice, this is not possible. The best solution can be the usage of operational amplifiers in a voltage follower configuration. By reducing the reference current to a very low level, its contribution to the EC current flow will become negligible. The counter electrode (CE) is typically made out of an inert material. It is important that the electrochemical (EC) reactions occurring on it, do not interfere with the WE. The accurate control and measurement of the potential between the working electrode (WE) and reference electrode (Ref), as well as the current flowing between the working electrode (WE) and counter electrode (CE), are achieved using a device known as potentiostat. Figure 1.2 shows a very simple schematic of a potentiostat[3].

At electrodes, two types of processes can take place: faradaic and non-faradaic currents. Adsorption/desorption without charge transfer and the formation of the electrical double layer (EDL) involve no charge transfer across the metal-solution interface and are referred to as non-faradaic processes. Despite no charge crossing the interface, external currents can still flow when there are changes in potential or solution composition, just like the charging of a capacitor without having a conductive path between the capacitor's plates. Processes involving charge transfer across the metal-solution interface are named faradaic processes. Electron transfer in faradaic processes induces oxidation or reduction, governed by Faraday's law. Consequently, the flowing current is directly proportional to the reaction rate. The half-reaction for reduction (forward) and oxidation (backward) is shown in Reaction 1.1 where n is the number of electrons transferred during the reaction. The potential at which this reaction is in equilibrium under standard conditions is the standard equilibrium potential

of Ox-Red couple with the notation of $E_{Ox/Red}^0$. The standard potential is referred to the normal hydrogen electrode (NHE), which has standard equilibrium potential of zero, by convention.



The Nernst equation (Equation 1.2) describes how the equilibrium potential E_{eq} of the Ox/Red electrode depends on the thermodynamic activities (a_{Ox} and a_{Red}) of its components.

$$E_{eq} = E_{Ox/Red}^0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} \quad (1.2)$$

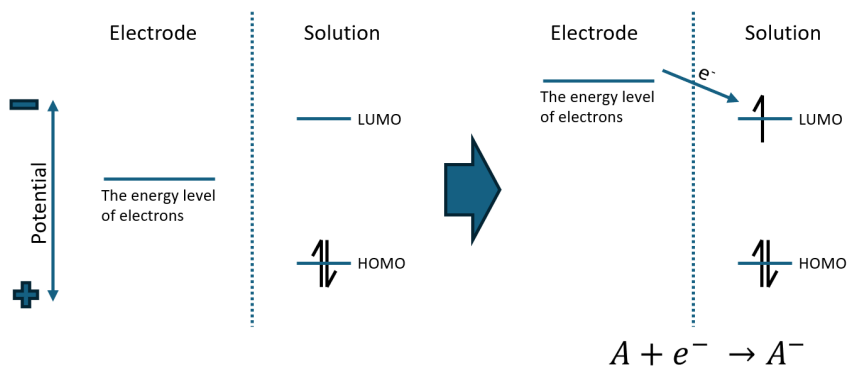
Where R , F , and T represent the universal gas constant, the Faraday constant and the temperature at which the reaction takes place. The thermodynamic activities of the species are usually replaced by their concentration, which is a reasonable approximation if the ionic strength of the electrolyte is low and constant. Thus Equation 1.2 can be rewritten as Equation 1.3, in which C_{Ox} and C_{Red} are the concentrations of the oxidized and reduced species.

$$E_{eq} = E_{Ox/Red}^0 + \frac{RT}{nF} \ln \frac{C_{Ox}}{C_{Red}} \quad (1.3)$$

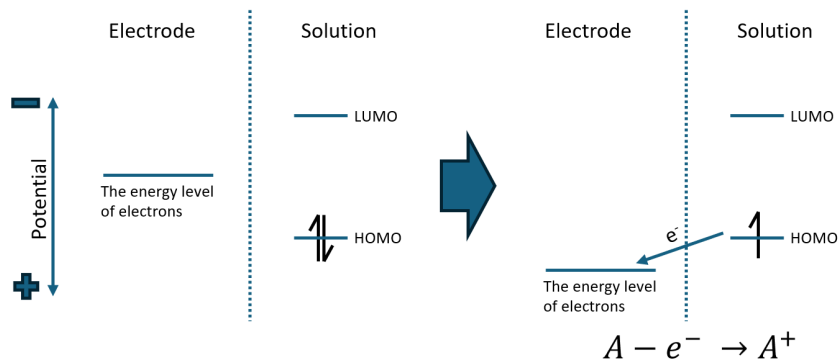
By applying a positive or a negative potential to the electrode, one can lower or raise the energy level of the electrons in the electrode. At a negative potential with respect to the equilibrium potential, electrons are thermodynamically favored to move from the electrode to occupy the lowest unoccupied molecular orbital (LUMO) of A in the electrolyte. As a consequence, A will be reduced to A^- and cause a negative current flowing in the system. By convention, if reduction takes place on an electrode, the electrode is called cathode and the corresponding reduction is named cathodic current. On the other hand, oxidation of A to A^+ will occur only if a potential positive with respect to the equilibrium potential is applied, thermodynamically favoring the electron to transfer from the highest occupied molecular orbital (HOMO) in the electrolyte to the electrode. The electrode is called anode and the corresponding positive current is the anodic current. This oxidation-reduction process is shown in Figures 1.3b and 1.3a respectively.

Many parameters play an important role in the kinetics of electrode reactions and the rate of electron transfer is just one of them. For instance, mass transfer limitations, and chemical reactions before and after the electron transfer, can also influence the overall rate. The rate constants for electron transfer at the electrode surface, are influ-

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(a)



(b)

Figure 1.3: a) Reduction and b) oxidation process of A in a solution. By changing the applied potential to the electrode, depending on the magnitude and the sign of the potential, the electron can either be taken from the highest occupied molecular orbital or it can be transferred into the lowest unoccupied molecular orbital.

enced by the applied potential. Recording the current as a function of the potential, typically represented as i-E curves, can help to obtain proper information about these processes. There are different types of EC experiments, classified by the parameter which is kept constant, controlled, and measured. By applying a constantly varying potential to the electrode and recording the current flow, so-called cyclic voltammograms (CVs) can be recorded. The rate of potential change is called scan rate and is defined by $s = \frac{dE}{dt}$. A cyclic voltammogram contains forward and backward scans. If only one scan direction is applied, the technique is called linear sweep voltammetry. At a sufficiently slow scan rate, the obtained i-E curve is called the polarization curve.

1.1.2 The place exchange mechanism in oxidation-reduction cycles

During oxidation-reduction cycles, electrode surfaces can change due to atomic rearrangements/replacements. One of the key processes responsible for these changes is the place-exchange mechanism, where metal atoms swap positions with oxygen-containing species (such as oxygen or hydroxide) during oxidation at high enough potentials. During the cathodic voltage sweep, these oxygen species are removed, but the displaced metal atoms often do not return to their original positions. This leads to irreversible changes in the surface, including adatom and vacancy island formation.

Understanding the effects of place exchange mechanism is critical for optimizing electrode materials in catalysis, energy storage, and corrosion resistance. For example, in fuel cells and electrocatalysis, surface restructuring can enhance or diminish catalytic activity, depending on the degree of atomic rearrangement. Similarly, in electrochemical sensors, surface stability is essential for maintaining consistent performance over time[5]. Experimental techniques such as electrochemical scanning tunneling microscopy (EC-STM)[6], electrochemical atomic force microscopy (EC-AFM)[7, 5], X-ray scattering (SXS)[8], and X-ray photoelectron spectroscopy (XPS)[9] have provided valuable insights into how place exchange occurs at the atomic level. However, challenges remain in fully controlling this mechanism to engineer more durable and efficient electrode materials. Researches aim to develop strategies for stabilizing surfaces during ORCs, minimizing unwanted structural changes, and enhancing electrochemical performance across various applications.

1.2 Scope of this thesis

During electrochemical experiments involving various techniques, the electrode surface may undergo minor or significant transformations. Monitoring these surface transformations in real time while the electrochemical reactions are in progress is the primary objective of this thesis. Specifically, we focus on the evolution of the Au(111) surface under different electrochemical conditions (e.g., various electrolytes, delays) by applying oxidation-reduction cycles. Through this study, we aim to gain deeper insights into the dynamic changes occurring on the electrode surface, which are crucial for understanding electrochemical processes and optimizing electrode performance. **Chapter 2** is devoted to the design of the electrochemical scanning tunneling microscope with the desired specifications. The mechanical parts and the electrical modules (like potentiostat, controller, and analog module) are shown and discussed. Supplementary information for the flow-cell design is available in **Appendix A**. In **Chapter 3**, we studied roughening of Au(111) single-crystal electrode in 0.1 M sulfuric acid during 200 oxidation-reduction cycles with the developed EC-STM. In these experiments, we applied two experimental procedures called "without holding the potential" and "with holding the potential". Holding the potential cause some delays during the ORCs and its effects were studied. Supplementary information for these experiments is available in **Appendix B**. In **Chapter 4**, we studied the effect of different concentrations of chloride in 0.1 M sulfuric acid during 200 ORCs. The studied concentrations of chloride are 50, 10, and 1 μ M. The surface reacts differently to these changes and in the lowest concentration, some surprising behavior was observed. Finally, **Chapter 5** is about roughening of Au(111) single-crystal electrode in 0.1 M HClO_4 as the result of ORCs. Au(111) surface reacted in three counter-intuitive and different manners. Some areas started to get roughened (similar to pure H_2SO_4), some regions started to get dissolved and form vacancy islands, and others did not go through major changes over the ORCs. The knowledge from Chapters 3 and 4 helps us to rationalize the unanticipated results. The provided supplementary information can be found in **Appendix C**.