

CHAPTER 3:

EXPERIMENTAL

3.1 Basic concepts of the experimental techniques

In this part of the chapter, a short overview of some phrases and theoretical aspects of the experimental techniques used in this work are given. *Cyclic voltammetry* (CV) is the most common technique to obtain preliminary information about an electrochemical process. It is sensitive to the mechanism of deposition and therefore provides informations on structural transitions, as well as interactions between the surface and the adlayer. *Chronoamperometry* is very powerful method for the quantitative analysis of a nucleation process. The *scanning tunneling microscopy* (STM) is based on the exponential dependence of the tunneling current, flowing from one electrode onto another one, depending on the distance between electrodes. Combination of the STM with an electrochemical cell allows *in-situ* study of metal electrochemical phase formation. XPS is also a very powerfull technique to investigate the chemical states of adsorbates. Theoretical background of these techniques will be given in the following pages.

At an electrode surface, two fundamental electrochemical processes can be distinguished:

3.1.1 Capacitive process

Capacitive processes are caused by the (dis-)charge of the electrode surface as a result of a potential variation, or by an adsorption process. Capacitive current, also called "non-faradaic" or "double-layer" current, does not involve any chemical reactions (charge transfer), it only causes accumulation (or removal) of electrical charges on the electrode and in the electrolyte solution near the electrode. There is always some capacitive current flowing when the potential of an electrode is changing. In contrast to faradaic current, capacitive current can also flow at constant

potential if the capacitance of the electrode is changing for some reason, e.g., change of electrode area, adsorption or temperature.

Under potentiostatic conditions, charging process tends to be very fast and resulting current will expire in a short time (usually a few milliseconds). It should be noted that in high resistance media, the capacitive current will need a substantially longer period to fall off. This time is proportional to the product of the resistance and capacitance (RC).

3.1.2 Faradaic Process

Faradaic currents are a result of electrochemical reactions at the electrode surface. From the position of the current peak (peak potential), the nature of the species can be deduced. Usually under potentiostatic conditions, faradaic currents are slower to diminish than capacitive currents. The scan rate should therefore be chosen slow enough to reduce the charging current, without letting the magnitude of the faradaic current decline below noise level. In case of fast scan rates, there might be an overlap with the capacitive current. Usually in these cases, one will employ a range of scan rate allowing for detailed analysis of the electrochemical components.

3.2 Electrochemical methods & Theoretical Backgrounds

3.2.1 Cyclic Voltammetry (CV)

To receive the preliminary information about a new system the cyclic voltammetry (CV) is nearly always the technique of first choice. The cyclic voltammetry can be applied for a study of all electrochemical reactions without limitations. With the help of this method, it is possible to get information about the type of reactions observed in the system and the potentials at which they occur. At the same time this technique is unfortunately not the best one to obtain quantitative data about electrochemical nucleation processes.

The three-electrode method is the most widely used because the electrical potential of reference does not change easily during the measurement. This method uses a reference electrode (RE), working electrode (WE), and counter electrode (CE) (also called the secondary or auxiliary electrode). Standard CV experiments consist of measuring the current flowing through the WE during a triangular potential perturbation. The applied potential is measured against the RE, while the CE closes the electrical circuit for the current to flow. The experiments are performed by a

potentiostat that effectively controls the voltage between the RE and WE, while measuring the current through the CE (the WE is connected to the ground).

Electrolyte is usually added to the test solution to ensure sufficient conductivity. The combination of the solvent, electrolyte and specific working electrode material determines the range of the potential to be applied.

Principle of CV:

Briefly, this method can be introduced as a reversal technique, which involves sweeping the electrode potential between two limits at a known sweep rate. At the beginning the working electrode is held at some potential, E_i , where no electrode reactions occur. During measurement the potential is swept linearly at a rate v between two limiting potentials E_1 and E_2 (Fig. 3.1 a). The same sweep rate is normally chosen for the forward and reverse sweep. The corresponding current is recorded as a function of the varying potential. A theoretical cyclic voltammogram for a reversible system is shown in Fig. 3.1 b. For the cathodic scan (applied potential is decreasing) the current has a negative sign, for the anodic scan (applied potential is increasing) the current has a positive sign.

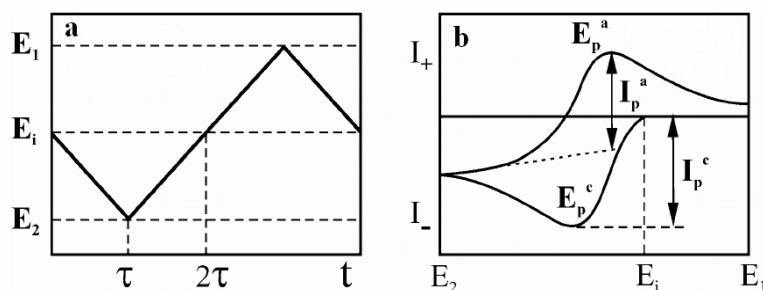


Figure 3.1 a) Potential sweep during cyclic voltammetric measurement; E_i is initial value, E_1 and E_2 are two limiting values. b) A typical cyclic voltammogram of a reversible reaction; anodic (a) and cathodic (c) processes, E_p is the potential at the current peak I_p .

3.2.2 Chronoamperometry

Chronoamperometry is very powerful method for the quantitative analysis of a nucleation process. This useful technique leads to obtain the initial information about nucleation and growth mechanism in a studied system. Additionally, the amount of charge for deposition (dissolution)

can be determined. Also, this method can be applied for the determination of a nucleation rate constant and an adsorption isotherm.

With the *chronoamperometry*, the current is measured versus time as a response to a (sequence of) potential pulse. The recorded current can be analysed and its nature can be identified from the variations with time. For example: at short times the capacitive current is dominant ($\propto e^{-t/RC}$; with R= solution resistance and C=capacitance) while at longer time scales, the diffusion limited faradaic current might prevail ($\propto t^{-1/2}$)^[103].

Principle of chronoamperometry

At the beginning of the transient experiment the potential of the working electrode is held at E_i (Fig. 3.2.a). At $t=0$ the potential is instantaneously changed to a new value E_1 , and corresponding current time response is recorded as shown in Fig. 3.2.b.

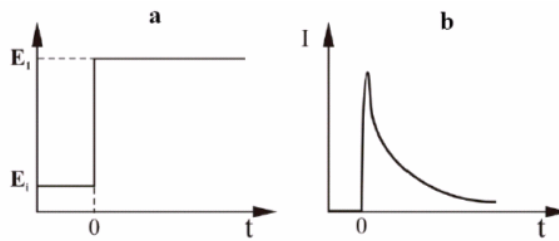


Figure 3.2 The chronoamperometric experiment. **a)** The potential-time profile applied during experiment, E_i is initial value and E_1 is the potential where no reduction of O occurs or some other potential of interest. **b)** The corresponding response of the current due to changes of the potential.

In order to determine the exact form of current-time dependence for a planar electrode the current density, Cottrell equation is used:

$$|I| = \frac{nF \sqrt{D_o} c_o^\infty}{\sqrt{\pi t}} \quad (\text{Eq. 3.8})$$

For *diffusion controlled process*, it can be noticed that the current falls as $t^{-1/2}$. This feature is frequently used as a test for this type of process and from the slope of I vs. $t^{-1/2}$ the diffusion coefficient D_o can be calculated^[103].

It is important, that such an analysis has to be applied over a broad time interval in order to ensure the reliability of results. At short times the current consists of a large nonfaradaic component due to charging of the double-layer capacitance. The non-faradaic current decays exponentially with time constant $R_u C_d$, where R_u is an uncompensated resistance and C_d is the double layer capacitance:

$$|I| = \frac{E}{R_u} e^{-t/R_u C_d} \quad (\text{Eq. 3.9})$$

Thus, the time constant $R_u C_d$ will determine the shortest time required to conduct the chronoamperometric experiment. Therefore, measurements should be performed for times which are much greater than $R_u C_d$. After passing the time equal to $R_u C_d$, the double layer capacitance is charged by 63 % and after $3R_u C_d$ by 95 %, see Eq. 3.9. Thus, knowing the time constant one can easily estimate the time needed for double layer charging ^[103].

At long time, however, the natural convection (may be caused by temperature and concentration gradients) comes into effect and diffusion in that case is not the only mode of the mass transport. Hence, the typical time range of chronoamperometric measurements lies normally in the range from 0.001 to 10 s. However, there are a number of additional instrumental and experimental limitations. For example, current and voltage characteristics of a potentiostat can limit the current maximum and time resolution.

Even though the chronoamperometry is relatively simple technique, there are a number of difficulties, which are related to the interpretation of the current-transient curve. Hence, it is very important to find the possibility of comparative analysis of the chronoamperometric results with the results of cyclic voltammetry and other techniques. This type of comparison will also help to understand the studied system more completely and with better precision.

3.2.3 AC Voltammetry

The measurement of the electrode capacity is known to provide direct information about the adsorption of surface electro-active molecules on the electrode surface. Most traditional differential capacitance techniques use phase-selective Alternating Current voltammetry (ACV) where a sinusoidal perturbation voltage at a fixed frequency is superimposed on the DC voltage of cyclic voltammetry (CV) (Fig. 3.3). The in-phase and quadrature components of the resulting AC current are measured as functions of the DC voltage, and the measured parameters are

converted to (voltage dependent) C_{diff} . If these measurements are performed at more than one AC frequencies, then the DC voltage scan of CV is repeated every time the frequency is changed. This approach only is practical for systems held in “long-term” stationary state that provide identical surface conditions in repetitive CV cycles and throughout the time (at least several minutes in most cases) necessary to complete the multiple DC scans. Many non-faradaic systems obey these criteria, but most faradaic reactions are associated with more complex, time dependent surface processes.

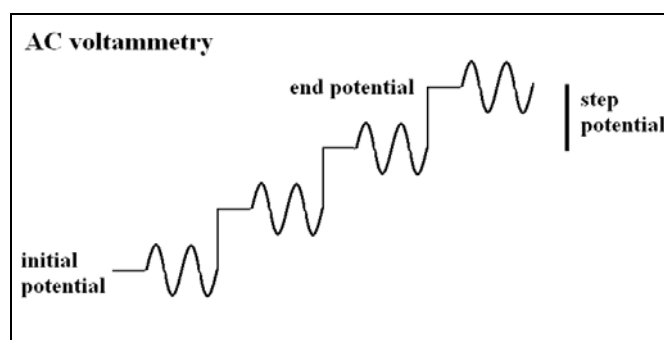


Figure 3.3: A schematic representation of AC voltammetry.

Usually, the studies aimed at determining the adsorption parameters of organic compounds on solid electrodes are performed with the AC impedance technique at a fixed frequency. These capacitance measurements are very useful to determine the values of the PZC due to the dependence of the capacitance on the frequency of the alternated potential applied.

In our experiments discussed here, the amplitude of the perturbation was 3 mV and the frequencies were typically between 20 and 200 Hz, depending on the experiment.

3.2.4 Electrochemical Scanning Tunneling Microscopy (EC-STM)

Scanning tunneling microscopy is based on the quantum mechanical effect of electron tunneling. Two electrodes (in the case of STM one of two electrodes is a metal tip and the second one is a conducting surface under study) are brought very close to each other and by applying a bias voltage (approx. several volts) between them, the tunneling current, typically on the order of a few nA, will flow and can be precisely measured. The arising current depends exponentially on the tip-surface distance. This property of the tunneling current plays the crucial role in STM and allows to control the sample-tip separation with high vertical resolution. An STM image is

obtained while the tip scans over the surface and corresponds quite closely to topography of the surface electronic states. Schematically, the principle of the STM is shown in Fig. 3.4.

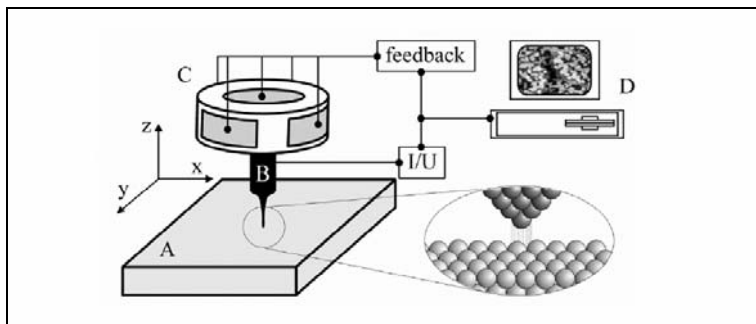


Figure 3.4: The principle setup of STM. The STM tip, **B**, scans over the substrate, **A**. The tip is connected to the piezo, **C**, which is controlled by feedback. The STM image can be obtained by holding the current, I , or bias, U , constant. The controller, **D**, governs the whole system and transforms the tunneling signal in a gray scale image.

3.2.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy known as XPS or ESCA (Electron Spectroscopy for Chemical Analysis) has been developed in the Fifties by Professor K. Siegbahn. The Physics Nobel Prize awarded his work in 1981. The most interesting thing with this technique is its ability to measure binding energy variations resulting from their chemical environment. This technique is able to obtain the chemical composition of various material surfaces up to 1 nm depth. Most of the elements can be detected except hydrogen and helium. For the past 20 years, this type of spectrometry emerged as a key tool in surface analysis, mainly because of two major features:

- Quantitative analysis
- Information on the chemical nature and state of the detected elements.

Photoemission principle: If one irradiates a sample with monochromatic X-rays (e.g., the Al- K_{α} line at 1486.6 eV, the Mg- K_{α} line at 1253.6 eV, or synchrotron radiation), electrons will be ejected from the sample into the surrounding vacuum. Some of these electrons are removed from the deep core levels of the atoms making up the lattice, and they are of particular interest of us. If the atoms are sufficiently close to the surface ($< 20 \text{ \AA}$), there is a high probability that the electrons will escape without being inelastically scattered and suffering the consequent loss in

kinetic energy. We are interested in the distribution of unscattered electrons vs. their kinetic energy in vacuo, that is, the photoelectron spectrum.

The sample is introduced in the first chamber (sample preparation chamber). This chamber is then pumped by high vacuum pumps (also called secondary vacuum pumps) down to a vacuum below 10^{-7} mbar. When the proper vacuum has been achieved, the sample is transferred into the analysis chamber and the XPS experiment may begin. The analysis chamber vacuum ranges from 10^{-8} mbar to 10^{-11} mbar.

The energy of the photon that ejects an electron must be conserved and can be separated into four terms:

$$h\nu = E_b + E_k + E_r + \Phi_{sp} \quad (\text{Eq. 3.10})$$

$h\nu$: X-ray beam incident energy, E_b : Electron binding energy inside the atom, E_k : Electron kinetic energy when leaving the specimen, E_r : Recoil energy (usually very small). Φ_{sp} : Spectrometer work function (3-4 eV).

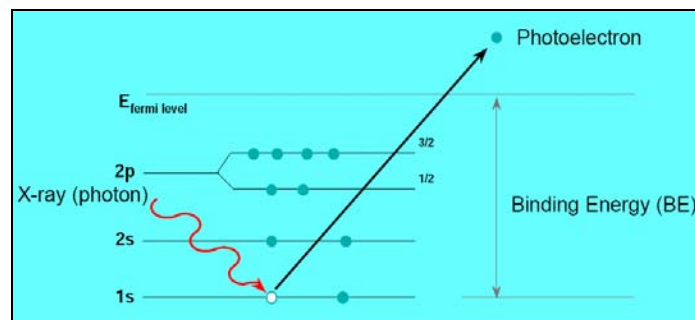


Figure 3.5: *The Photoemission process.*

From an analytical point of view, the utility of XPS is that it provides atomic information about the surface region without seriously damaging. Some information about the oxidation states is also available, because the binding energy of an electron in a given orbital is affected slightly by its electronic environment. Thus, one can see, for example, separate peaks for 1s electrons derived from nitrogen in its amide and nitro forms.

XPS signals can be detected for atoms throughout the periodic table, except helium and hydrogen. The sensitivity limits are on the order of 0.1 atomic percent, except for lighter elements, which are often detectable only above 1 to 10 %.

Recently, considerable attention has been devoted to the phenomenon of UPD of metal adatoms and the nature of the interaction between the adatom and the substrate. For example, one can see that the binding energy of Cu-2p_{3/2} electrons for Cu adatoms on Pt differs markedly from the value for bulk copper. The negative shift in binding energy suggests that the deposited copper is not in an oxidized form, but instead is metallic atom in a distinctive electronic environment^[44].

3.3 Instrumentation & Experimental Setup

In this part the experimental equipments, which have been used in the course of this work are introduced.

3.3.1 Potentiostat

A potentiostat is a device used to keep a working electrode (WE) at desired potential with respect to a reference electrode (RE). This is done by a current which is passed from the working electrode to a counter electrode (CE). The arrangement of the potentiostat and the electrodes is sketched in Fig. 3.6 b. From a more electronic point of view, a potentiostat is a special kind of feed-back amplifier. The potentiostat used in this work was an Autolab PGSTAT12 (Eco Chemie B.V.) equipped with a GPES 4.9 software.

3.3.2 The Electrochemical Cell

A conventional three-electrode electrochemical cell was employed in our studies (Fig. 3.6 b). The cell is surrounded by a glass jacket allowing water circulation to keep the temperature of the electrolyte at a specified value. Julabo F32 thermostat was used to control the temperature. The electrochemical experiments were always performed at 20 °C. The electrolyte was purged with pure Argon to remove dissolved oxygen at least 20 min. During the experiments, argon was passed over the electrolyte without disturbing the meniscus configuration of single crystal.

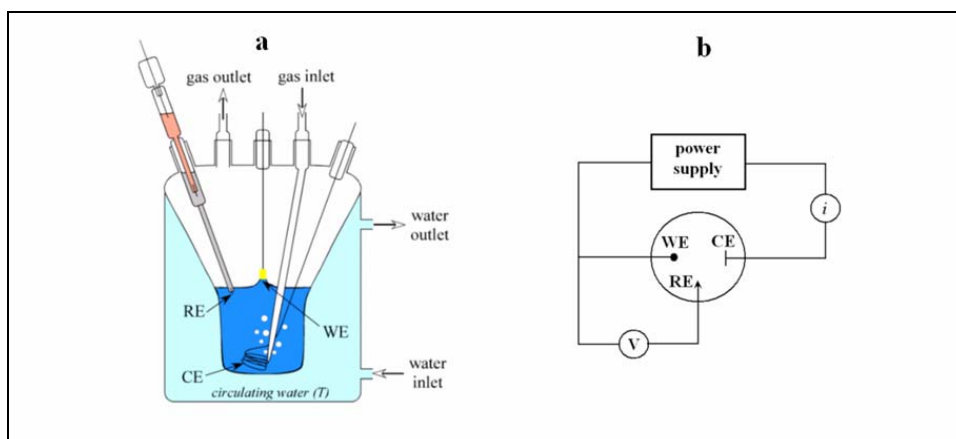


Figure 3.6.a-b: Typical three electrode electrochemical cell and notations: WE: working electrode, CE: counter electrode, and RE: reference electrode.

The cell was cleaned with the vapor of boiled nitric acid at least three days afterwards rinsed thoroughly with three-distilled water prior to experiment. The Faraday cage was employed to avoid outside electrical field disturbance and electrically connected to the ground.

3.3.3. Electrodes

3.3.3.a Working Electrode (WE)

We have used two different cylindrical gold single crystals during the electrochemical experiments ($2r = 5$ mm) and STM studies ($2r = 10$ mm) as working electrodes. The advantages of using gold single crystal can be counted as having a chemically inert and structurally well-characterized surface, besides these, making the samples easy to prepare as well as comparatively uncomplicated handling. The crystals were grown, cut, and polished by MaTecK in Jülich, Germany. To obtain large terraces the crystal was flame-annealed several times in a Bunsen burner until having a light red color and cooled in an Argon atmosphere before each experiment, touched to the electrolyte under potential control in hanging meniscus configuration to let connection with only (111) face of the crystal.

The typical cyclic voltammogram of Au(111) in aqueous 0.1 M HClO₄ electrolyte is shown in Fig. 3.7 a. Obtaining this characteristic voltammogram indicates the perfectness of crystal surfaces, cleanliness of the cell used and quality of the reference electrode. It is in good agreement with the previously reported voltammograms^[68, 104]. In Fig. 3.7 b, capacity-potential

curve of the electrolyte of 0.01 M HClO₄ on Au(111) is given. The minimum at the capacity around -0.22 V is the PZC of Au(111) electrode.

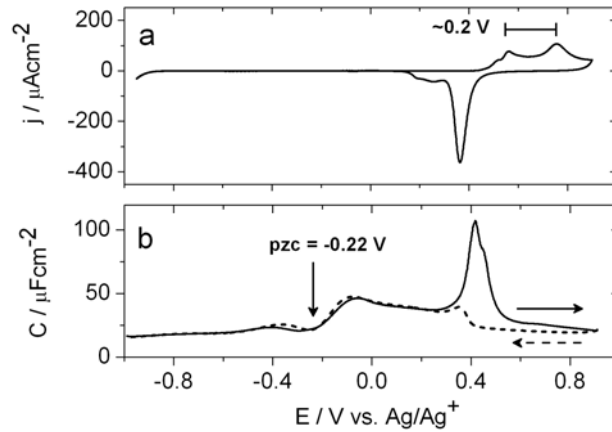


Figure 3.7.a: Typical cyclic voltammogram of Au(111) electrode in 0.1 M aqueous perchloric acid solution. Sweep rate: 50 mV/s. **b:** Capacity-potential curve for Au(111) in 0.01 M aqueous perchloric acid solution. Perturbation frequency and amplitude when measuring the capacity curve: 80 Hz, and 3 mV, respectively.

The typical STM picture of Au(111) surface taken in 0.1 M HClO₄ electrolyte shows the existence of large terraces and well-defined steps (Fig. 3.8). The length of the terraces varies between 300-600 nm and the height of steps changes between 0.25 nm and 0.85 nm corresponding to mono-atomic and three-atomic heights, respectively.

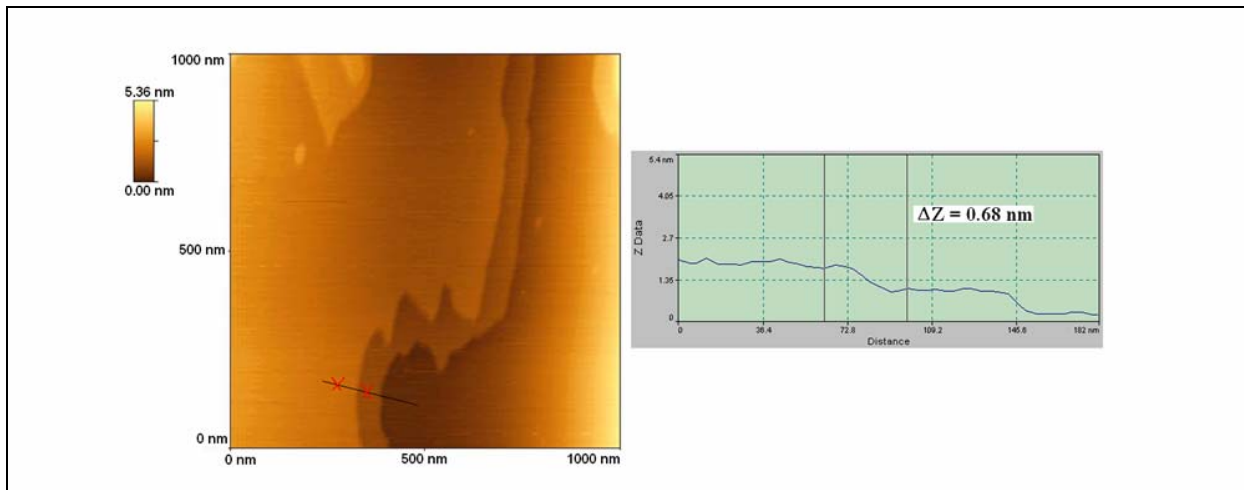


Figure 3.8: The STM picture ($1 \times 1 \mu\text{m}^2$) of bare Au(111) electrode in 0.1 M HClO₄ electrolyte. $V_{\text{appl.}} = 0$ mV, $V_{\text{bias}} = 10$ mV, $i_t = 2$ nA.

For XPS investigations, thin gold film (200-300 nm thickness, 11x11 mm) deposited on a quartz plate (Arrandee) were used as the working electrode. Under the Au film a very thin (~ 2 nm) layer of chromium is deposited, which improves adhesion of the gold to the quartz. Before the preparation of sample in electrochemical cell, gold film substrate was flame annealed to have excess (111) terraces.

3.3.3.b Reference Electrode (RE)

The purpose of the RE is to provide a stable, reproducible voltage to which the WE of an electrochemical cell. Ideally, if a small current is passed through the electrode, the potential change is negligible, and in any case, returns to the initial value when the current ceases. In addition, the potential value should not vary with time and should be reproducible from electrode to electrode.

Ag/Ag⁺ (0.1 M) reference electrode with a potential of 0.741 V vs. NHE was used in our study (Fig. 3.9). Prior to preparation of RE, the pure silver wire (1 mm, 99.9 %) was cleaned with a special solution containing hydrogen peroxide (30%) and ammonia (25%) for few minutes, until the silver wire becomes completely bright, then put in contact with a platinum wire and dipped into a 0.1 M aqueous solution of silver perchlorate and 0.1 M perchloric acid.

To separate the reference electrode and the cell, a salt-bridge containing 0.1 M HClO₄ solution was employed aiming to avoid the contamination from trace amount of the specifically adsorbing agents. The salt bridge was made from a Duran glass with a platinum wire molten at the tip. A ring crevice between the glass and the platinum allows a negligible leakage by, which prevent change of the electrolyte pH.

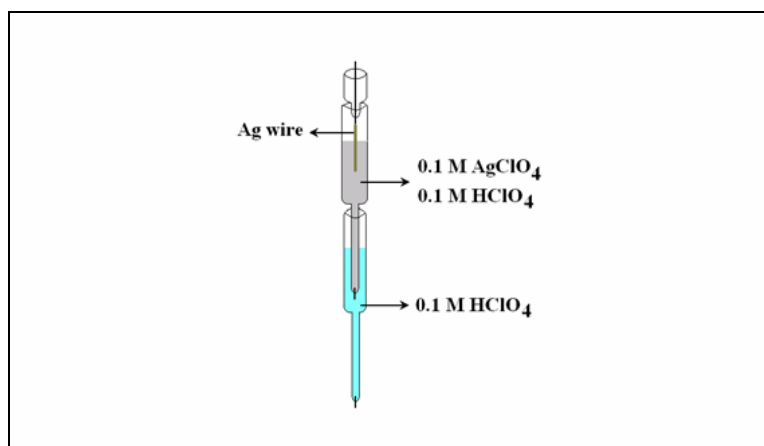


Figure 3.9: *Ag/Ag⁺ reference electrode*

3.3.3. c Counter Electrode (CE)

The role of the counter electrode (CE) is to supply the current required by the working electrode, without limiting the measured response of the cell. The processes occurring on the counter electrode is not considered; it is usually made of inert materials (noble metals or carbon/graphite) to avoid its dissolution. It should have a large area compared to the working electrode. A gold wire c.a. 0.5 mm thick and 200 mm long served as CE in this work (see Fig. 3.6 a).

3.3.4 XPS investigations

Ex situ XPS measurements were carried out using synchrotron radiation at the end-station SurfCat (Optics-beamline, PM-4) at BESSY, Berlin, Germany. Excitation energies were 1150 and 630 eV depending on the experiment. The ultrahigh vacuum (UHV) system consisted of interconnected load-lock, sample preparation and analysis chambers (base pressure: 2×10^{-10} mbar). Sample transfer between the chambers proceeded without breaking UHV conditions. Photoemission spectra were collected with a hemispherical electron energy analyzer (Scienta SES 100) set to an energy resolution of 140 meV (80–20% intensity drop at the Au Fermi edge) under normal emission. The angle between incident ultraviolet light and the energy analyzer was constant at 60°; and all spectra were recorded at normal emission. In order to determine the sample work functions the secondary electron cutoff was recorded with the sample biased at -10 V to clear the analyzer work function.

Batch-processing of UNIFIT 2005 program was used for evaluation of spectra. Background was calculated using Shirley type subtraction procedure and the fitting procedure for curve syntheses was carried out by convolution of Lorentzian and Gaussian functions. Peak positions were calibrated using the Au-4f_{7/2} peak (84.00 eV).

3.3.4.a Transfer procedure

The sample was transferred from the electrochemical cell to the UHV pre-chamber at different steps as follows:

- (i) The electrochemically prepared sample was emersed from the electrolyte under potential control and afterwards disconnected from the voltage source under argon atmosphere. During this step the electrochemical double layer at the surface is frozen [105]
- (ii) The electrode surface was washed with three-distilled water to remove anions and metal ions from the surface whose signals can overlap with surface species in the UHV experiments. Electrochemically, during this procedure we change the pH value as well as the potentials distribution at the surface. But according to the respective Pourbaix diagram the silver species should be stable in this pH range.
- (iii) The sample is fixed on a sample holder and grounded on top by screws with the UHV instrumentation. The potential of the sample is now the ground of the instrumentation. Therefore, any electrochemical memory does not longer exist.

3.3.5 EC-STM measurements

The in situ STM measurements were carried out with a Topometrix Discoverer 2010. The electrochemical setup consisted of a Jaissle BI-Potentiostat PG 100, an AMEL 568 Function Generator and a home-built cell made of KEL-F. The Au(111) working electrode was a single crystal disc with a diameter of 10 mm and a thickness of 2 mm, which was supplied by MaTeck (Juelich, Germany). The electrode was flame-annealed for about five times before the experiment. A platinum wire was used as counter electrode. The selfmade reference electrode (Ag/Ag⁺ electrode) was connected by a salt-bridge containing a solution of 0.1 M HClO₄. The cell, the working electrode and the counter electrode were cleaned in a concentrated solution of nitric acid and were then purged with three-distilled water. As STM tips we used tungsten wires with a diameter of 0.25 mm, which had been etched in a solution of 2 M NaOH. The tips had been purged with three-distilled water and were immediately electroplated with a thin gold layer. As coating we used Apiezon wax. All STM images had been done in constant current mode.

3.4 Chemicals and Solutions

Thymine and adenine (99 %, Aldrich) were dissolved by stirring. Sodium perchlorate (Merck, p.a, 0.06 M) was used as supporting electrolyte salt. Argon (4.8, Messer) was used for

deaeration of the electrolyte. The other chemicals are listed as following: silverperchlorate-monohydrate (99.999 %) (Aldrich), perchloric acid (suprapur, Merck), copperperchlorate (99.999 %, Alfa-Aesear), nitric acid (Merck, 65% suprapur). All solutions were prepared using triply distilled water, and the chemicals were used as received without further purification.