
CHAPTER 3: EXPERIMENTAL

3.1 THE ELECTROCHEMICAL CELL

Figure 3.1 shows a sketch of the electrochemical cell used in this thesis. It consisted of a glass cell surrounded by a glass jacket in which water is circulated in order to allow temperature control by means of a thermostatic bath (Julabo, F32). A conventional three-electrode arrangement was employed and the electrolyte was purged with argon before each measurement for at least 30 minutes aiming at assure an oxygen free environment. During the experiments, argon was passed over the top of the electrolyte in order to avoid any external disturbance of the meniscus configuration (s.b.).

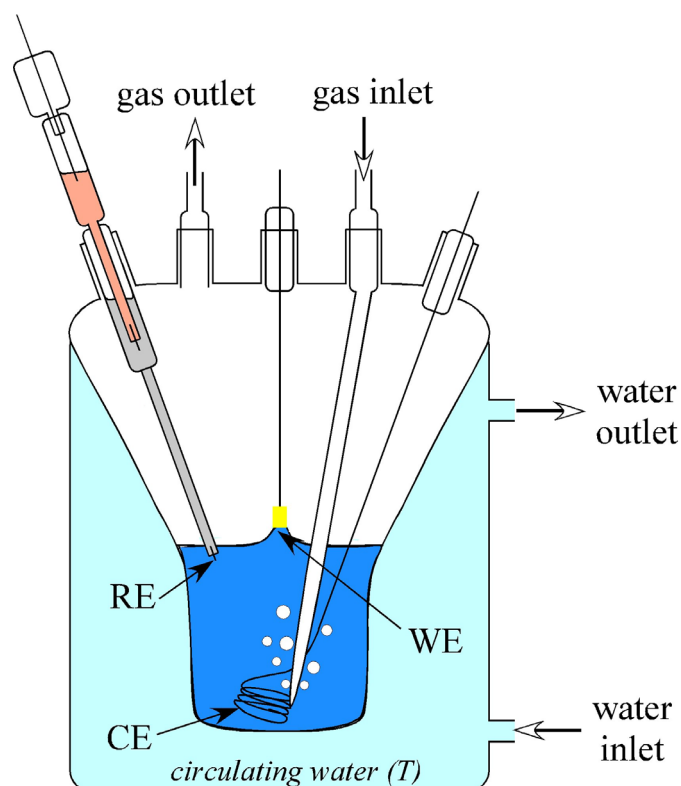


Figure 3.1: Electrochemical apparatus. WE: working electrode, CE: counter electrode, and RE: reference electrode.

The cell was cleaned with hot nitric acid during at least three days and then rinsed thoroughly with supra pure water prior to each experiment.

A Faraday cage, i.e., a conductive enclosure surrounding the electrochemical system, was employed to reduce current noise (picked up on the working electrode) and voltage noise (by the reference electrode). The Faraday cage was electrically connected to the ground.

3.2 ELECTRODES

3.2.1 WORKING ELECTRODE (WE)

The working electrode (WE) is the one at which the electrochemical process of interest takes place. The interfacial studies of the present thesis were carried out with a gold (111) single crystal (Mateck, $\varnothing = 5$ mm) electrode with geometric area of 0.19 cm^2 and the current density values reported throughout this thesis are referred to this value. Prior to each experiment, the WE was flame annealed in a Bunsen burner for some seconds and then cooled in an argon atmosphere as suggested earlier [61]. This procedure was repeated for several times and after that the WE was immediately transferred to the electrochemical cell. Finally, the WE was brought in contact with the electrolyte solution through the so-called hanging meniscus configuration [62], in order to isolate the face of interest.

The quality of the Au(111) surface and the cleanliness of the electrochemical apparatus can be inferred from the cyclic voltammogram depicted in Figure 3.2. This experiment was obtained in a 0.1 M perchloric acid aqueous solution and the main features of the current-potential profile are in fair agreement with the previously reported (see, for instance ref. [63]).

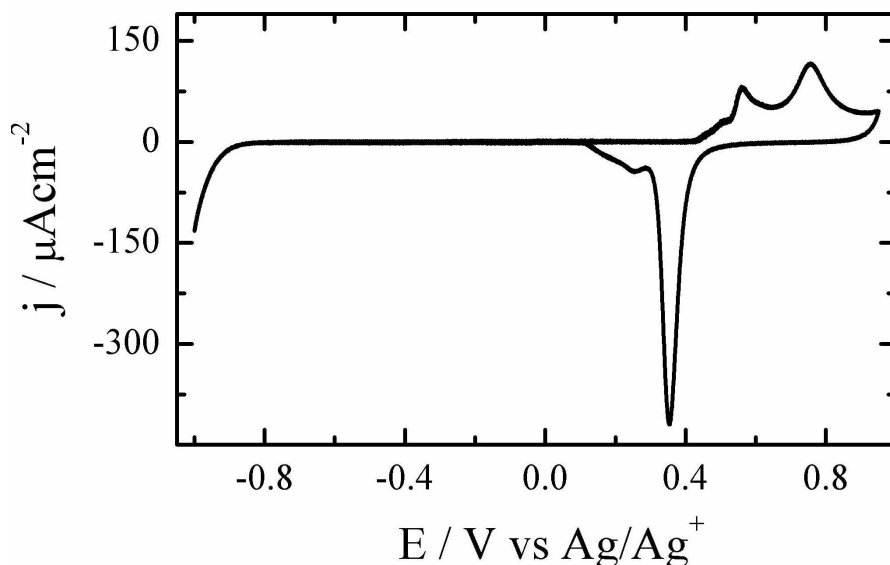


Figure 3.2: Typical voltammetric behavior of Au(111) electrode in aqueous perchloric acid (0.1 M) electrolyte solution. Sweep rate 50 mV s^{-1} and $T = 20 \text{ }^\circ\text{C}$.

3.2.2 REFERENCE ELECTRODE (RE)

The role of the reference electrode (RE) is to provide a fixed potential to which the potential of the WE is referred. The RE is sometimes called ideal nonpolarizable electrode [38] once even when a current of few microamperes is passed, its potential remains nearly unperturbed.

An Ag/Ag^+ reference electrode was used during all measurements reported here and was prepared as follows. A silver wire (0.5 mm) was first cleaned with a solution containing one part of hydrogen peroxide (30%) and three parts of ammonia (25%) for few minutes, until the silver wire becomes completely bright. The silver was then put in contact with a platinum wire and dipped into a 0.1 M aqueous solution of silver perchlorate and 0.05 M perchloric acid.

The RE was placed in an external compartment and connected to the electrochemical cell (c.f. Figure 3.1 above) via a salt-bridge, which was filled with a 0.1 M aqueous perchloric acid solution. The salt bridge consisted of a Duran glass with a platinum wire molten at the tip, in order to facilitate the contact of the solutions by a ring crevice between the glass and the platinum. By using such a configuration, leaking of perchloric acid into the cell is negligibly small, which prevent change of the electrolyte pH.

3.2.3 COUNTER ELECTRODE (CE)

The purpose of the counter electrode (CE) is to supply the current required by the working electrode, without limiting the measured response of the cell. In this sense, it should not impose any characteristics on the measured data, and as consequence 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 Figure 3.1).

3.3 CHEMICALS AND SOLUTIONS

The supporting electrolyte used in most of the experiments discussed here was a (0.1 M) aqueous solution of sodium perchlorate (Merck, p.a.) and, when necessary, the pH was adjusted by adding a certain volume of a (0.1 M) aqueous solution of perchloric acid (Merck, 70% serape.) or of a (0.1 M) aqueous solution of sodium hydroxide (Merck, suprapur). The other chemicals used are listed as follows: thymine (Fluka, $\geq 97\%$), adenine (Fluka, $> 99.5\%$), guanine (Fluka, $> 99\%$), bromouracil (Merck, $> 98\%$), argon (4.8, Messer), nitric acid (Merck, 65% suprapur). All solutions were prepared using triply distilled water, and the chemicals were used as received, without further purification. Owing to its low solubility, guanine dissolution was assisted by heating and stirring.

3.4 INSTRUMENTATION AND TECHNIQUES

Due to the similarity of the electrochemical conditions with charged biological interfaces, the adsorption behavior of many organic molecules such as nitrogen bases and their derivatives can be investigated via different electrochemical methods, making this system very attractive. In this section, after some technical details of the potentiostat used in our experiments, a brief overview of the different electrochemical techniques used in the present work is given.

3.4.1 POTENTIOSTAT

A potentiostat is an instrument that allows the control of the potential between the WE and the RE, whereas the electric current flowing through the WE and the CE is independently measured. Since the potential of the RE remains virtually constant during the experiments

(s.a.), the potential control acts directly across the WE/electrolyte interface. The potentiostat used in this work was an Autolab PGSTAT30 (Eco Chemie B.V.) equipped with a GPES 4.9 software.

3.4.2 CYCLIC VOLTAMMETRY

The most common technique to study electrode reactions is cyclic voltammetric. Cyclic voltammetric experiments consist of applying a linearly varying potential between the WE and the RE and simultaneously measuring the current flowing across the WE.

The general view of a cyclic voltammetric experiment is given in Figure 3.2 in terms of the perturbation (upper part) and system's response (lower part). In this figure the perturbation is represented by a triangular wave form of the applied potential in time, which involves sweeping the electrode potential between the cathodic, E_c , and anodic, E_a , limits at a constant sweep rate. In its turn, the system's response is given in terms of current density/applied potential curves, which display the general information of interfacial processes as a function of the applied potential.

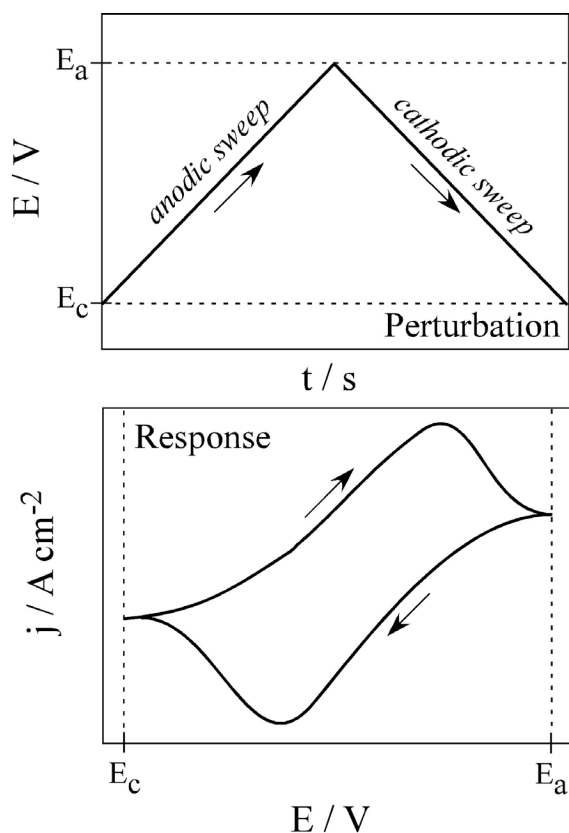


Figure 3.3: Scheme of cyclic voltammetric experiments illustrating the perturbation (upper plate) in the form of linear potential ramps and the system's response in terms of the current density/potential profile.

3.4.3 CHRONOAMPEROMETRY

The study of the variation of the current response after a single potential step under potentiostatic control is called chronoamperometry. The system's response, i.e. the current density/time trace following the potential step (from E_i to E_f) perturbation, is schematically given in Figure 3.3.

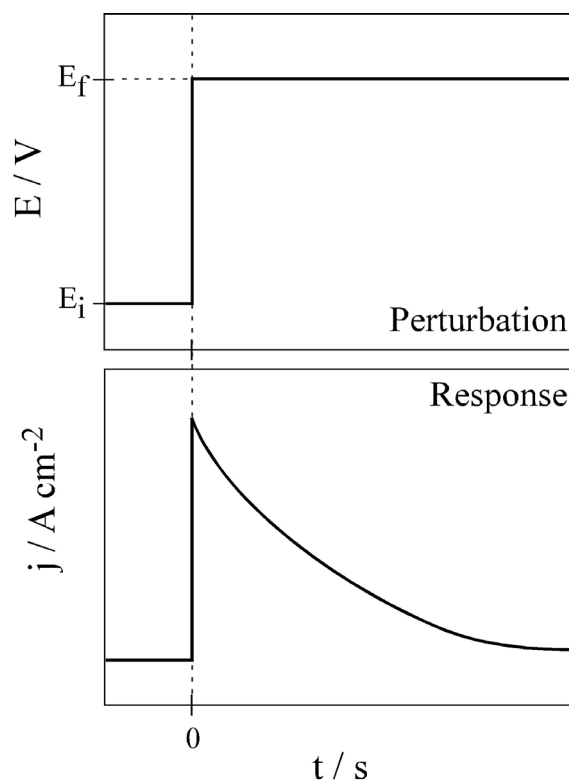


Figure 3.4: (upper plate) Perturbation in the form of a potential step from E_i to E_f , and (lower plate) current density evolution response in a chronoamperometry experiment.

In this work, the I vs. t profiles were used to investigate the formation and dissolution kinetics of the physisorbed and chemisorbed thymine film on gold electrode. In the case for the physisorbed formation film, the potential was stepped between an initial potential (E_i),

where is assumed that no adsorption takes place, to a various final potentials (E_f) into the region at which physisorbed film was known to form. For the dissolution of the chemisorbed film, E_i was placed at positive potential, were the surface was completely covered by the film, and stepped into region III and II (E_f).

The shape of the obtained I vs. t transient curves provided a deeper understanding of the processes involved in formation and dissolution of these films as adsorption/desorption, condensation (in the case of film formation) and the double-layer charging.

3.4.4 CAPACITY CURVE

The measurement of the electrode capacity is known to provide direct information about the adsorption of surface electro-active molecules on the electrode surface. In this method, a sinusoidal, small amplitude, potential perturbation applied during the potential scan and the alternating current vs. potential curve is registered. In the experiments discussed here the amplitude of the perturbation was 3 mV and the frequency was typically between 20 and 100 Hz, depending on the experiment.