
CHAPTER 3: EXPERIMENTAL

In this chapter, all topics concerning the experimental part of this thesis are presented. For the sake of conciseness, some basic concepts about the electrochemical experimental setup were omitted, they can be found in conventional electrochemistry textbooks [66, 67, 69-71, 138].

3.1 ELECTRODES

3.1.1 WORKING ELECTRODE (WE)

The working electrode (WE) is the one at which the electrochemical reactions under investigation take place. In the present work a polycrystalline platinum electrode was employed as WE. It consists of a ring-shaped electrode (inner and outer diameters were 30 and 32 mm, respectively) embedded into a Teflon cylinder and placed at the top of the electrochemical cell (see Figure 3.1 below). Only ca. 2 mm of the Teflon body was immersed into the electrolyte. Furthermore, in all experiments reported here the WE was rotated.

Prior to each experiment, the WE was subjected to a systematic pre-treatment in order to assure clean experimental conditions and, as a consequence, reproducible results. Such pre-treatment consists of an electrode surface polishing on cloth carbon pad impregnated with abrasive diamond paste (Ernst Winter) down to a particle size of $0.25\ \mu\text{m}$. Before transferring to the electrochemical cell, the electrode was placed in an ultrasonic bath a few times in order to eliminate any residues from the mechanical polishing. Once transferred to the cell, the electrode was ‘electrochemically annealed’ [118], that is, cycled between 0.05 and 1.4 V (vs. RHE) at $0.1\ \text{Vs}^{-1}$ in 0.5 M H_2SO_4 electrolyte solution under N_2 bubbling for ca. 1 h.

3.1.2 COUNTER ELECTRODE (CE)

The purpose of the counter (or auxiliary) electrode (CE) is to supply the current required by the WE without limiting the measured response. In this way, the CE should have a large area compared to the WE. In the context of electrochemical spatiotemporal pattern formation, as already stressed in the second chapter, the CE position with respect to the WE and reference electrodes is very important. This fact calls for a precise CE placement in the cell. In the experiments shown throughout this work, a 1 mm thick Pt wire bent to a ring of 65 mm in diameter was fixed 40 mm from the WE (see Figure 3.1 below) and served as CE. Furthermore, in some experiments the distance between the CE and the WE was varied by employing a similar CE mounted to a glass capillary in the same way as the adjustable RE was positioned (s.b.).

3.1.3 REFERENCE ELECTRODE (RE) AND POTENTIAL PROBE (PP)

The reference (or indicator) electrode (RE) provides a fixed potential which does not change during the experiment, in other words, it is independent of the current flowing through the system (or, more precisely, between WE and CE). Usually such device is referred to as an ideal nonpolarizable (or depolarizable) electrode [67]. In potential controlled experiments, the applied voltage between the WE and the RE is controlled by a potentiostat, and since the voltage drop across the RE/electrolyte interface is constant, any change in the applied voltage through the cell appears directly across the WE/electrolyte interface (assuming an ohmic potential drop through the electrolyte can be neglected).

Either a mercury-mercurous sulfate ($\text{Hg}/\text{Hg}_2\text{SO}_4$) electrode or a silver-silver chloride (Ag/AgCl) electrode was used as RE. The $\text{Hg}/\text{Hg}_2\text{SO}_4$ RE was placed in a separate compartment external to the main cylinder of the cell and is referred hereafter as external RE. The external compartment was connected to the main cylinder of the cell below to the plane of the CE. The other RE was put into a J-shaped glass capillary (Haber-Luggin capillary), placed between the WE and the CE, and its position was varied along the central axis symmetrically to the center of the WE.

The interfacial potential near the ring-shaped platinum WE was monitored by using a potential probe, PP, consisting of a Ag/AgCl electrode inside a J-shaped glass capillary. The tip of this PP was placed at 1 ± 0.2 mm below the Pt ring. Since during the experiments the WE was rotated at 20 Hz, and the voltage between PP and WE was measured with an acquisition rate of 1 kHz (i.e. 50 points/rotation), it was possible to reconstruct the spatiotemporal picture of the interfacial potential in front of the WE.

All potentials in the present work are given with respect to the reversible hydrogen electrode (RHE).

3.2 ELECTROCHEMICAL CELL AND GENERAL SETUP

Figure 3.1 depicts the experimental cell used in this work. It consisted of a cylindrical glass cell of 400 cm^3 in volume. The electrolyte could be purged with another gas inlet tube placed at 180° to the one shown in order to assure symmetry of the gas distribution inside the

cell. Using a glass cylinder in the cell bottom prevented the presence of hydrogen bubbles at the electrode surface.

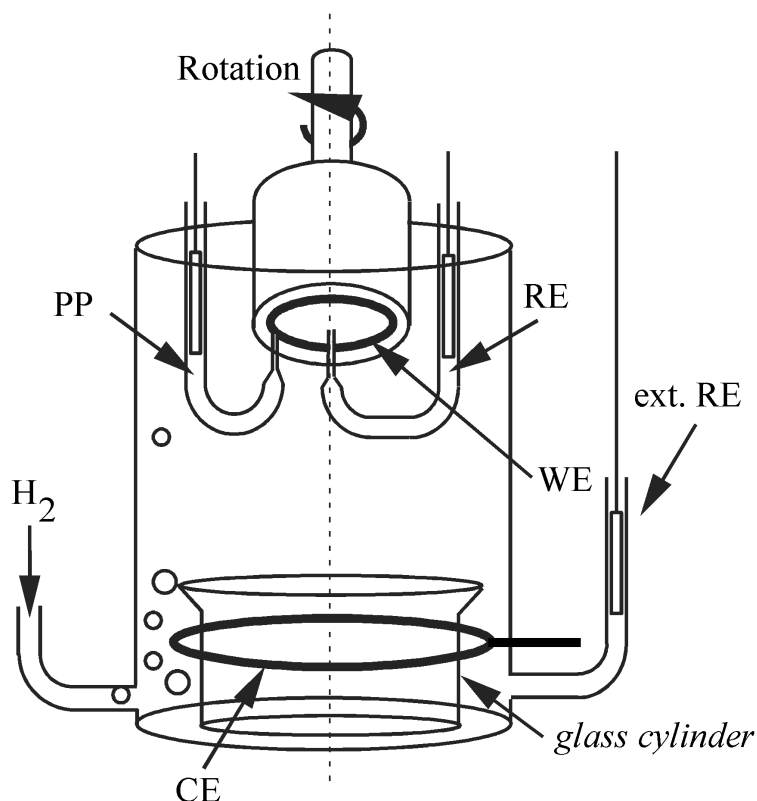


Figure 3.1: Electrochemical cell used in the experiments.

In the experiments discussed in chapter 7, section 7.1.1, item (a), a slightly different electrochemical cell was used. This cell is almost identical to the one just described. The only appreciable difference of this cell is in the porous glass wall in the tubes through which hydrogen was supplied. Owing to this difference, for a similar H_2 flux, smaller bubbles were produced in this cell, leading to a slightly different convection of the electrolyte.

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

3.3 CHEMICALS AND ELECTROLYTE SOLUTIONS

All chemicals (H_2SO_4 , HCl , and $CuSO_4$) were purchased by Merck (p.a. grade) and used as received. Solutions were prepared using supra-pure water (Millipore Milli-Q water

system, 18 M Ω cm). The gases N₂ and H₂ (5N, Linde) were supplied to the electrochemical cell without any further purification or treatment. The supporting electrolyte, diluted H₂SO₄, was prepared from concentrated H₂SO₄ and supra-pure water (Millipore Milli-Q water system, 18 M Ω cm).

3.4 INSTRUMENTATION AND TECHNIQUES

3.4.1 POTENTIOSTAT

A potentiostat is an instrument that allows one to select and control the voltage between the WE and the RE, whereas the electric current through the WE and the CE is independently measured. The potentiostat system FHI – G050 – 1 designed by D. K. Roe [139, 140] and manufactured at the electronic laboratory of the Fritz Haber Institut was used in the present work. Like conventional commercial instruments, this potentiostat can electronically compensate the electrolyte resistance between the WE and the RE up to 100 Ω [139]. In order to compensate higher values of the electrolyte resistance, another device that mimics a negative impedance was connected between the WE and the potentiostat and used in some experiments (see chapter 6 for further details).

3.4.2 ROTATING SYSTEM

An important aspect to be taken into account in the experimental design is to provide a means by which mass transport of species to and from the electrode surface can be controlled in a precisely known way. In electrochemical systems a usual procedure to control and *vary* the mass transport conditions is to work under forced convection environment provided by rotation of the electrode or by impinging the solution to the electrode surface. Under forced convection conditions, the current density can be significantly increased with respect to its value in a stationary electrolyte. Moreover, as far as nonlinear dynamics is concerned, it is known that mass transport of reactants/products to/from the reaction plane in front of the WE is an important process which has to be taken into account in the description of the system. Slow mass transport can, for instance, turn a bistable system into an oscillatory one.

In all experiments discussed throughout this thesis, the WE was rotated at 20 Hz. Under these conditions forced laminar convection was established and efficient mass transport was assured. Besides the reasons referred to in the previous paragraph, the rotation of the WE had a particular importance here, because it was exploited to measure the interfacial potential along the WE. As discussed in section 3.1.3, the radial distribution of the interfacial potential along the WE was measured by means of a stationary potential probe placed near the WE. Considering the WE rotation rate of 20 Hz and a sampling rate of 1 ms it was possible to measure the interfacial potential with a resolution of 50 points along the ring. In the context of electrochemical pattern forming systems, another way to obtain spatiotemporal resolution of the interfacial potential distribution along quasi one-dimensional electrodes employs a stationary WE and several potential probes close to the WE [43, 44, 141-151], frequently using solution stirring to improve mass transport conditions. In terms of the potential distribution along ring-shaped electrodes, when compared to our strategy, this approach has basically two disadvantages: hardly controllable mass transport and smaller resolution of the potential distribution, which is intrinsically limited by the number of probes.

In this work the analytical rotator model AFMSRX from Pine instruments⁵ was used. It allows rotations within the range from 50 to 10,000 RPM (or equivalently from ca. 1 to 165 Hz), but in the setup used in the present work became mechanically unstable for rotation rates > 20-25 Hz.

The precise angular position was followed independently by monitoring a transmitted optical signal in the rotating connecting rod. More precisely, an optical signal was sent through the transparent connecting rod and the transmitted signal was registered at the opposite side by means of a photocell. A small piece of tape was attached to the transparent rod such that it inhibited the light from passing through the rod. The generated optical pattern was then recorded and used to correct any angular drift in the potential probe signal.

3.4.3 NEGATIVE IMPEDANCE DEVICE (NID)

The cell resistance, R_{Ω} , was partially compensated either by changing the position of the RE (see Figure 3.1) or by means of an externally connected electronic device that acted as

a negative resistor. The compensating effect of such a ‘Negative Impedance Device’ (NID) when placed between the WE and the potentiostat is illustrated in Figure 3.2. These tests were done by connecting a dummy cell to the potentiostat, whereby the uncompensated resistance between the WE and the CE was set to $1100\ \Omega$ (solid line in Figure 3.2).

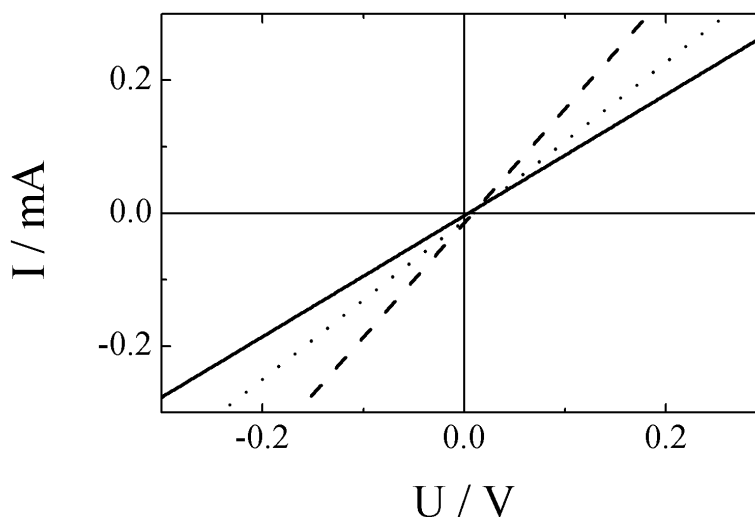


Figure 3.2: I/U characteristics of a dummy cell ($R_{\text{dummy}} = 1100\ \Omega$) under potentiodynamic control (solid line) and the effect of the NID with $R_{\text{NIC}} = -250\ \Omega$ (dotted line) and $-500\ \Omega$ (dashed line). The compensating effect is seen in the change of the I/U slope.

In chapter 6, the main aspects of the NID used will be discussed in more depth. Finally, it should be mentioned that the resistance values mentioned in this work were measured by perturbing the system with a high frequency (10 kHz) low amplitude (10 mV) sinusoidal potential perturbation in a region of zero faradaic current, taking advantage of the fact that at sufficient high frequency, the double layer impedance is close to zero and thus the total impedance is close to the uncompensated cell resistance.

⁵ See product brochure at: <http://www.pineinst.com/>.