
Chapter 2: Experimental Setup and Materials

2.1 Electrochemical cell and electrode setup

Figure 2.1 depicts the experimental cell for (a) ring electrode and (b) ribbon electrode used in this work. A cylindrical glass vessel of approximately 100 mm in inner diameter and 120 mm in height with gas inlets near the bottom was used as electrochemical cell. All electrode connections were mounted into the Teflon cap of the cell which also accommodated the capillary tubes serving as local potential probes. The glass tube was mounted into the Teflon lid of the cell fixing the working electrode at a variable height within the electrolyte.

A polycrystalline Pt ring and ribbon electrode were used as working electrode. The tip of a thin Pt wire (0.3 mm in diameter and embedded in a 4 mm glass tube except for the 3 mm tip) was welded onto the Pt ring at the point near the outer edge to provide a connection of the Pt ring to the outer circuit; in case of Pt ribbon electrode, the tip of thin Pt wire was welded on the center of Pt ribbon. A platinized Pt wire (1 mm in diameter) bended to a ring (65 mm in diameter) served as counter electrode and placed concentrically about 80 mm above the Pt ring; in case of Pt ribbon, two Pt coils with thickness of 1 mm were used as counter electrode and placed about 80 mm above the Pt ribbon. The reference electrode compartment was also connected *via* a Luggin-Haber capillary.

Eleven (or twelve) glass capillaries as local potential probes of approximately 200 μm inner diameter and 110 mm length were located close to ring electrode with a distance of approximately 1 mm; in case of the ribbon electrode, eight glass capillaries were used. The upper ends of the capillaries were attached to glass tubes of 8 mm inner diameter

which hosted the Hg/Hg₂SO₄ reference electrodes. The glass bodies of the local potential probe electrodes were filled with a highly concentrated electrolyte solution (0.5 M Na₂SO₄) prior to air-free insertion. Finally, an additional Pt wire sealed in a glass tube except for a 2 mm tip was mounted into the cell. This electrode serves as ‘pulse electrode’ for the application of controlled spatially inhomogeneous perturbations of the potential distribution near the working electrode. This Pt tip was approached to the upper face of the working electrode up to about 2 mm.

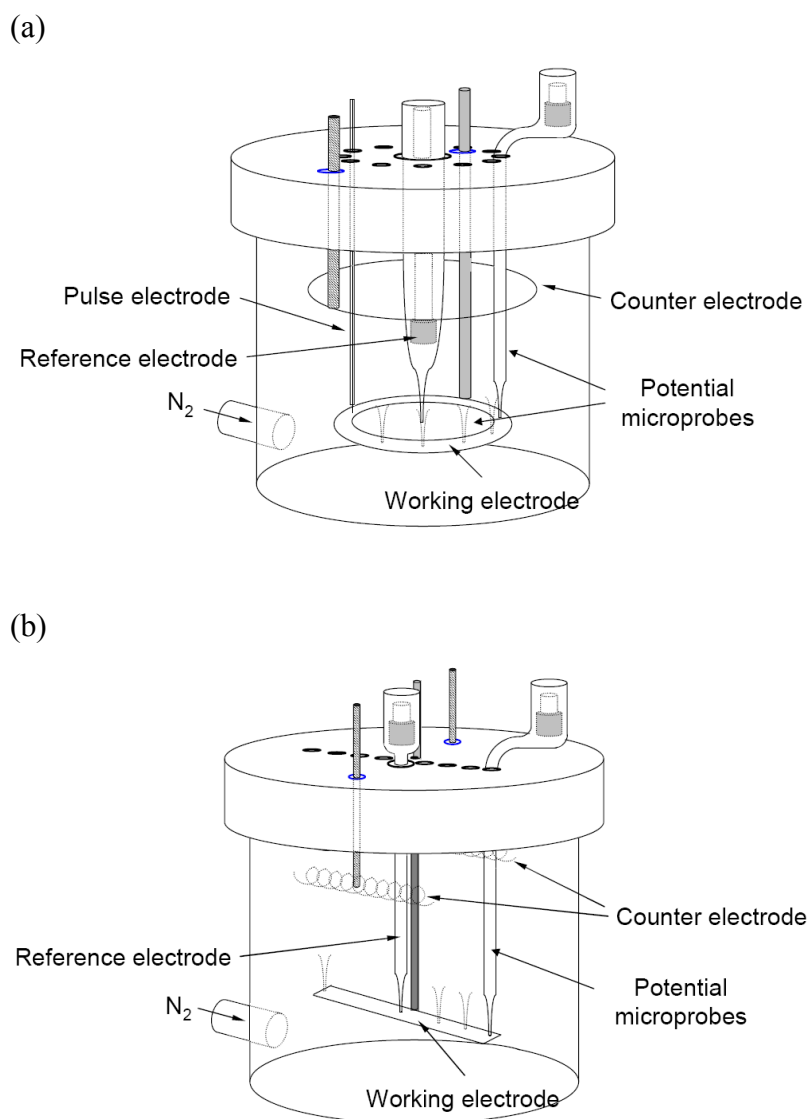


Figure 2.1. Electrochemical cell for (a) ring and (b) ribbon electrode used in the experiments.

2.2 Electrodes

2.2.1 Working electrode

In the present work a polycrystalline Pt electrode was employed as working electrode. In chapter 3, 4 and 6 ring-shaped electrode (34 mm inner diameter, 40 mm outer diameter and thickness of 0.25 mm) was used to investigate the different spatiotemporal pattern formation of interfacial potential. In chapter 5 ribbon-shaped electrode (width of 4 mm, length of 58 mm and thickness of 0.25 mm) was used also.

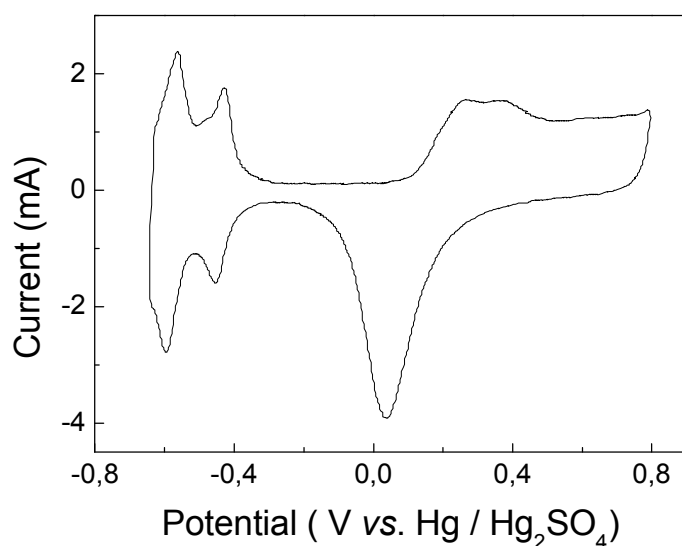


Figure 2.2. Pt ring working electrode was electrochemically annealed. Potential is cycled between -0.65 V and $+0.80$ V (vs. Hg/Hg₂SO₄) at 0.1 V/s in 0.5 M H₂SO₄ electrolyte solution under N₂ bubbling.

Before each experiment, the working electrode was chemically cleaned in a mixture of conc. sulphuric acid (H₂SO₄, suprapure) and hydrogenperoxide (H₂O₂, 30%). Then a voltammetric curve between -0.65 V and $+0.80$ V (vs. Hg/Hg₂SO₄) was recorded in 0.5 M H₂SO₄ deaerated by N₂ to verify initial cleanliness as shown in Figure 2.2. A well defined peak pair of oxidation/reduction of platinum electrode around $+0.10$ V and $+0.30$ V was found, which indicated that the platinum electrode had smooth and clean surface [59].

2.2.2 Reference electrode

The reference electrode 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 working electrode and counter electrode). In all experiments, a Hg/Hg₂SO₄ reference electrode (Radiometer Corp.) was employed; its use proved to be convenient, since most systems studied throughout this thesis were operated in acidic solvents containing high sulphate concentrations (SO₄²⁻). Thus, leakage problems or ionic impurities stemming from the reference compartment were negligible.

2.3 Electrolyte solution

All solutions were prepared using ultrapure water (Millipore Milli-Q water system, 18 MΩ·cm). Prior to all experiments, solutions were purged with high-purity nitrogen (Linde Technische Gase) in order to remove dissolved oxygen. In many experiments, the cell was kept under a nitrogen atmosphere during experiments to avoid oxygen diffusion into the solution. For all experiments involving formic acid oxidation, a deaerated solution mixture of 0.1 M HCOONa (Merck, p.a.) and 0.033 M H₂SO₄ (Merck, suprapur) was employed as the electrolyte.

A 1×10⁻³ M Bi³⁺ containing solution was prepared by dissolution of high-purity Bi (III) oxide (Bi₂O₃, Strem Chemicals Inc., 99.9998 %) in 0.5 M HClO₄ (Merck, suprapur). Appropriate amounts of the 1×10⁻³ M Bi³⁺ solution were added to the main electrolyte to obtain final concentrations of 1×10⁻⁶ M Bi³⁺. After the experiments, the working electrode was treated in conc. HClO₄ (Merck, suprapur) in order to completely remove only Bi residuals.

2.4 Experimental methods

2.4.1 Potential microprobe measurements

Potential microprobes have been used for quite sometime in order to measure the spatiotemporal evolution of the potential drop near the working electrode. As early as 1951,

Franck [8] studied activation fronts in one spatial dimension with three stationary probes, Lev *et al.* [11] measured the spatiotemporal potential using 15 electrode probes. In an elegant experiment, Flätgen [14, 15] used just one stationary potential microprobe on a rotating ring electrode and measured one-dimensional images of the interfacial potential at the ring electrode.

The potential microprobes consisted of a reference electrode, *e.g.*, Hg/Hg₂SO₄, mounted in a glass tube which terminated in a small capillary. The glass tube was filled with an electrolyte solution. These potential microprobes were used for the measurement of the potential distribution with negligible current flowing through the capillary. Figure 2.3 shows the setup of potential microprobes used for a ring electrode in the present work.

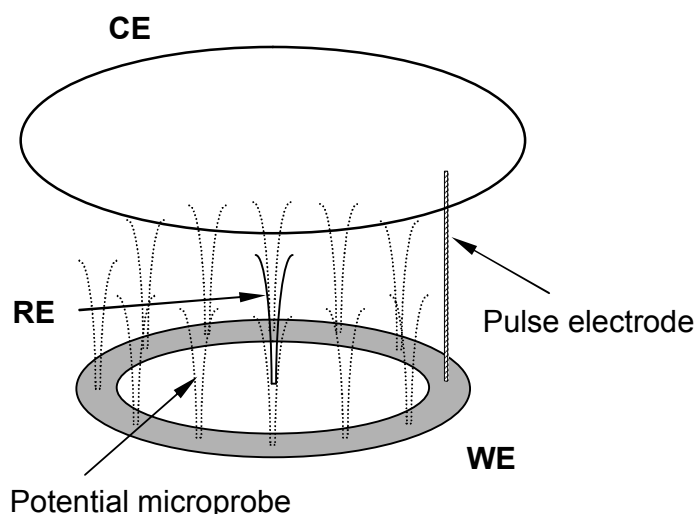


Figure 2.3. Potential microprobe setup for the measurements of evolution of the potential inside the electrolyte near the ring working electrode.

In some experiments, an additional Pt wire sealed in a glass tube for a 2 mm tip was mounted into the cell. This electrode served as ‘pulse electrode’ for the application of a controlled spatially inhomogeneous local perturbation of the potential distribution near the working electrode. This Pt tip was approached to the upper face of the working electrode to about 2 mm.

2.4.2 Apiezon wax coating

In order to avoid an additional effect of inhomogeneous electrical fields at the platinum ring and ribbon working electrode during the measurement, Apiezon wax was used to coat the connecting part between the working electrode and the wire encapsulated by glass.

In chapter 6, Apiezon wax was used to insulate parts of the surface of the ring electrode. Well-defined insulated areas were made by a coating of Apiezon wax using a template and a fine brush. It could be removed by dissolution in Trichlorethylen (C_2HCl_3).

2.5 Instrumentation and data processing

2.5.1 Potentiostat / galvanostat

Beginning in the 1950's most electrochemical experiments have been done with three electrodes and instrumentation built around a potentiostat which is an instrument to control the potential between a working electrode and a reference electrode by automatically varying the current between working and counter electrode in a three electrode system. A common design based on an operational amplifier [60] is shown in Figure 2.4. It ensures a true reference electrode, *i.e.*, very little current is drawn in this part of the circuit. A counter (auxiliary) electrode is used to pass the bulk current. The positive input is at 0 V (ground).

The current is measured by means of another operational amplifier attached to the indicator electrode lead. Since the input resistance is high, all current must flow through the resistance R_2 . However, the high gain of the amplifier produces an output voltage such that the potential at the inverting input is 0 V. Thus, the working electrode is held at 0 V as well, and the output potential is $-IR_2$, which is proportional to the cell current. The potentiostat mostly used in this work was built by the Electronic Lab (ELAB) of the Fritzy-Haber-Institute. The circuit is based on the idea of D. Roe [60].

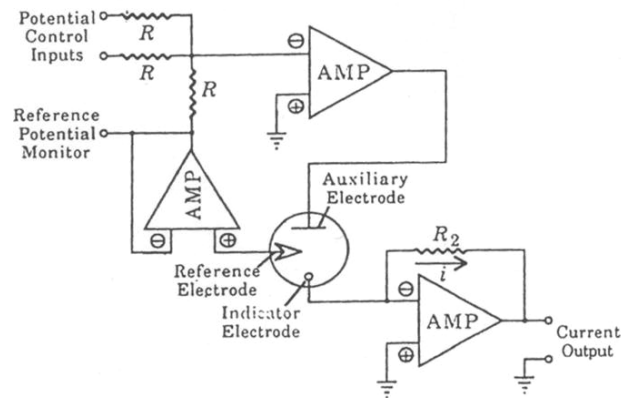


Figure 2.4. Potentiostat circuit for control of working electrode (indicator electrode) potential in a three electrode cell. Cell current is monitored with a current follower circuit, and the reference electrode is protected from excess current flow by an electrometer.

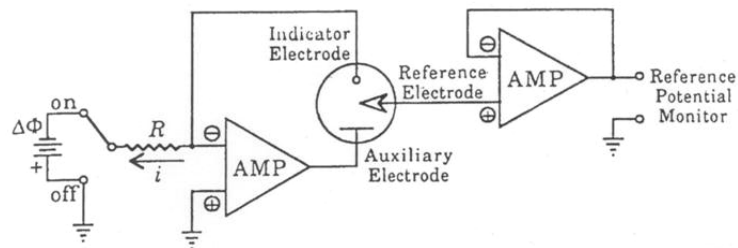


Figure 2.5. Galvanostat circuit for control of current through the cell.

In galvanostatic experiments, a constant current is passed through the cell, and the potential of the working electrode is monitored using a reference electrode. An operational amplifier circuit which performs this function (a galvanostat) is shown in Figure 2.5. Since the operational amplifier input resistance is high, the cell current must flow through resistor R . Feedback through the cell ensures that the working electrode stays at ground potential. Thus, the potential drop across the resistor is equal to the battery potential and the cell current is $I = \Delta\Phi/R$. For the galvanostatic measurements, an EG&G bi-potentiostat / galvanostat served as power source.

2.5.2 Data acquisition

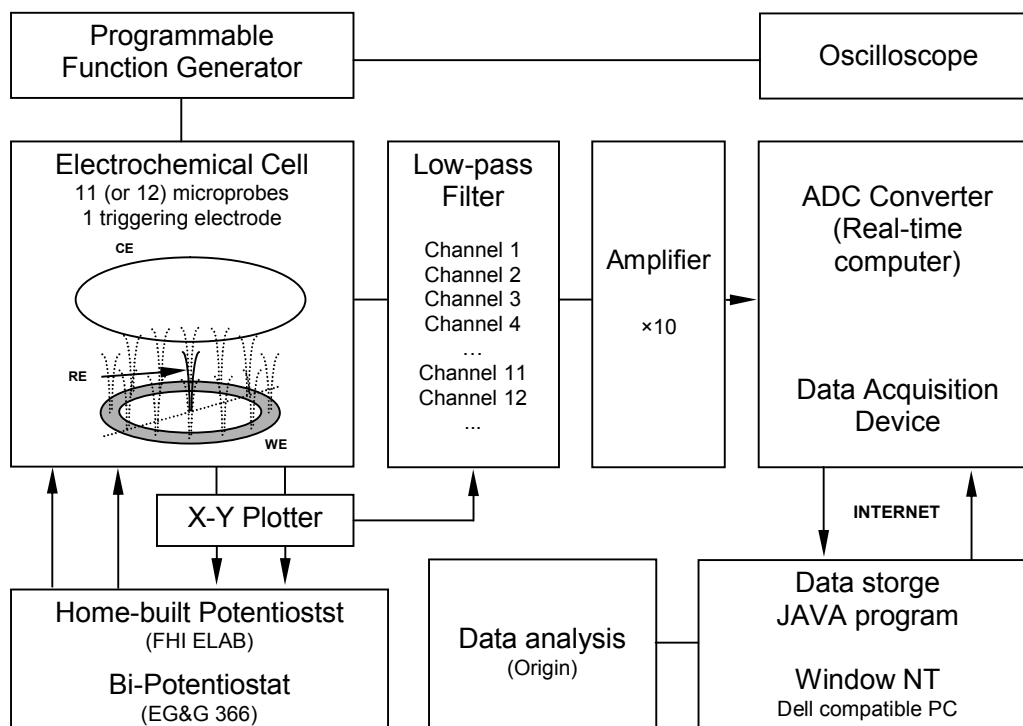


Figure 2.6. Principal experimental setup for data acquisition during multi-potential probe measurements.

The principal elements involved in the complete experimental cell and data acquisition setup are shown in Figure 2.6. Working, counter and reference electrode were controlled by the potentiostat / galvanostat the output of which was put on an X-Y recorder. The local potential probes were connected through a combined low-pass filter/floating-ground amplifier ($\times 10$, ELAB of FHI, Figure 2.7 shows the circuit) to the input channels of a 12 bit-16 channel multiplex A/D converter. During measurements, the digital information was stored temporarily in the data acquisition device before it was passed on to a permanent storage (personal Computer, Dell, Pentium 200 MHz) after completion of the measurement. The pulse perturbation electrode was connected to a programmable function generator (HM 8130, HAMEG) providing rectangular potential pulses of various amplitude and duration.

The JAVA measurement software (Computational Center of FHI) was executed from the PC, this software was connected to the acquisition device (CPU with DNS entry

'link') by pressing 'connect'. Upon starting the acquisition mode (START button), the 16-channel information was read into the temporary memory and transferred to the PC's hard disc after termination (STOP button). An ASCII file including the information was subsequently created with 16 columns and the number of rows equaling the number of multiplexed inputs. Being ASCII, the information was easily retrievable. The recording frequency could continuously be varied between 10 and 1000 Hz.

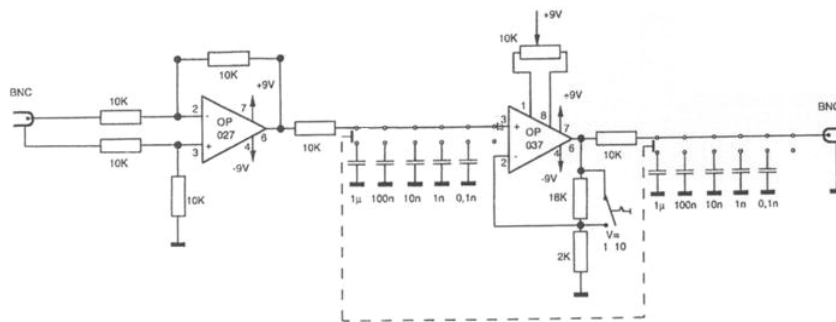


Figure 2.7. Electronic circuit of the amplifier with floating ground used for the spatially resolved measurements of the local potential drop at the electrode surface. Adapted from ELAB of Fritz-Haber-Institut.

