

Microelectrochemistry: Localized Monitoring of Passivity and Corrosion

M. M. Lohrengel, A. Moehring, and M. Pilaski

*Institute for Physical Chemistry and Electrochemistry
Heinrich-Heine-University Duesseldorf, 40225 Duesseldorf, Germany*

Electrochemistry is a very surface sensitive method but the bad lateral resolution had to be overcome. Recently developed micro techniques enable an application of the complete range of common potentiostatic and galvanostatic techniques together with a high spatial resolution.

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1. Introduction

Electrochemistry is extremely surface sensitive. This is caused by the large numerical value of Faraday's number and, hence, electrochemistry can detect and identify parts of a monolayer. The area of investigations is, however, typically around some cm^2 , i.e. the results are mean values of the complete surface rather than local data. In the last 40 years miniaturization became more and more important and, therefore, this discrepancy between normal resolution (less than nm) and lateral resolution (some cm) had to be overcome.

Miniaturization started with electronic equipment (chips, passive elements, connectors, switches), but later other technical systems like sensors, motors, and gears were also miniaturized (micro-mechanics). But even macroscopic technical parts are non-homogeneous: polycrystalline materials consist of grains of different crystallographic orientations which have a strong influence on the mechanical properties. Altogether modern technologies offer a wide range of components with micro-structured surfaces. Accordingly we must expect a non-homogeneous distribution of electrochemical behavior. A typical example is corrosion: it may occur homogeneously, but in many cases local corrosion occurs (pitting or crack corrosion) which weakens parts locally. Other examples are gas evolution (e.g. hydrogen or oxygen) or passivation which depends on the crystallographic orientation of the surface. All this demanded: the development of spatially resolved electrochemical techniques.

This general trend had already changed electrochemistry. Many new micro-techniques were developed by making components of electrochemical cells or complete

cells smaller and smaller.

2. Microtechniques

Thin film cells are used for more than 40 years. They were derived from macrocells by reducing of the electrode distance down to some μm . This decreased the cell volume so that *Faradatic* processes at the working electrode caused notable concentration changes.¹⁾

The miniaturization of the working electrode leads to microelectrodes,²⁾ nowadays with diameters down to some 10 nm.

More important for corrosion monitoring is a surface analysis with increased lateral resolution³⁾ This is realized by completely different techniques.

One method to reduce the wetted area of a macroscopic electrode is the partial coverage with insulating paints or resins. This means a *mask technique* with a fixed mask. Typical applications are the insulation of cutting edges or back-sides of sheet electrodes or the embedding of wires to get well defined surfaces. An interesting method to form structures on planar electrodes is the modification of photo resins by a focused laser beam⁴⁾ and subsequent electrochemical modification. This process is somewhat time-consuming, furthermore the developing process of the resin can produce artifacts on the surface. A quick method to address special parts of an planar electrode is the use of mobile masks. The problem, however, is seepage because the *mobile masks* show typically weak adhesion and thus prevent a precisely limited access to the surface. Mobile masks with repeated patterns in the μm range can be easily produced by LIGA-technology in metal or plastics⁵⁾ and allow the parallel processing of hundreds

or thousands of spots.⁶⁾

More common is the use of scanning probes⁷⁾:

*Scanning Kelvin probes*⁸⁾ measure the potential distribution of the sample surface in a non-contact mode, typically with resolutions in the μm range.

*Scanning reference electrodes*⁹⁾ detect the potential distribution in the electrolyte close to the interface.

Ion sensitive capillary electrodes measure the concentration of special ions. Originally, they were introduced to measure the concentrations of e.g. Na^+ , K^+ , Mg^{2+} , Cl^- in living cells in biology, but are also used to measure the distribution of concentrations close to the electrode during technical electrolysis.¹⁰⁾

Scanning microelectrodes (SXM¹¹⁾), especially the *Scanning Tunnel Microscope* (STM¹²⁾) measure the topography with a resolution in the atomic scale in a non-contact mode or, similarly, the *Atomic Force Microscope* (AFM) with a probe touching the surface, which also measures the local hardness of the sample.

The *Scanning Electrochemical Microscope* (SECM) was introduced by Bard *et al.*¹³⁾ It consists of a microelectrode above the sample. The distance is typically some μm . The diameter of the insulating material surrounding the microelectrode is larger than this distance (typically 5 to 10 times). Therefore, due to the flat cylindrical geometry a mass exchange by diffusion between of the microelectrode and the bulk of electrolyte is hindered.

Focussed radiation, e.g. *focussed laser beams*,¹⁴⁾ enable the determination of local photocurrents.

A special technique is *microellipsometry*¹⁵⁾ which allows the identification of thin surface films down to monomolecular layers.

However, all these methods have their special limits. A potentiostatic control is usually realized with STM, SECM, and focused laser beams only. Furthermore, the probes are commonly used in macrocells with electrode dimensions in the range of cm^2 and the complete sample is in contact with the electrolyte.

But there are good reasons to miniaturize not only single components but complete electrochemical cells.¹⁶⁾ Microcells must be used in applications where space is limited.

Electrochemical microsensors measure the concentration of soluble substances in liquid media, typically in macroscopic volumes. The sensor is separated from this larger volume by a selective barrier, often a membrane. Microbatteries are simply small devices for energy storage in miniaturized electronic equipment. Analytical microcells (e.g. in chromatography) are used to determine concentrations within the cell, usually by electrochemical¹⁷⁾ or spectroscopic methods. Flow-through microcells are used for pre-concentration of substances (stripping tech-

niques) or to get a fast response if the concentration changes with time. Non-flow microcells allow an analysis of small electrolyte samples.

The volume of a microcell is limited by different principles:

- by a hindrance of diffusion, e.g. SECM,
- by the electric field, e.g. in weakly conductive electrolytes,
- by the interface aqueous electrolyte/oil. This technique avoids evaporation of the solvent and is mainly used in biology [e.g.18].
- By an insulating solid material (e.g. glass or plastic, resin *etc.*),
- or by the interface electrolyte/gas. This is true for droplet cells where the volume is defined by the surface tension of the electrolyte and the contact angles.

In the next section we will focus to the last two methods.

Surface analysis with electrochemical methods is based on few fundamental techniques. Nowadays potentiostatic techniques are preferred. Depending on the shape of the potential-time-curve three fundamental techniques can be distinguished, *potentiodynamic sweeps* if the potential is changed with a constant rate, *potentiostatic pulse techniques*, if the experiment starts at a constant potential and is changed by step or impedance techniques. In this case the potential is modulated by a continuous wave (sine, triangle or square), typically in a frequency range from 1 MHz to 1mHz. This last technique requires a special equipment and a linear response of the system which is realized by small signal amplitudes.

We wanted to use these well established methods in microcells and, hence, had to retain the potentiostatic 3-electrode arrangement. This required the development of a new class of microcells.¹⁹⁾

3. Scanning droplet cells

A convenient and simple method for electrochemical surface analysis is to position small electrolyte droplets on the surface of interest and forms the cell (e.g.²⁰⁾). The wetted area defines the working electrode, this means the droplet diameter defines the resolution. Reference and counter electrodes must be added to get the 3-electrode arrangement. There are two variants where the electrolyte volume is limited either by surface tension (free droplet) or by a silicone rubber gasket.

The free droplet technique²¹⁾ is usually combined with gold capillaries (fig. 1). The gold capillary acts at the same time as the counter electrode and as the *Luggin* capillary of the reference electrode. In a typical arrangement the gold capillary has an outer diameter of 150 μm and a

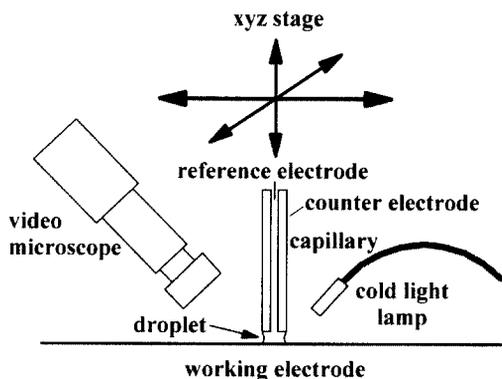


Fig. 1. Fundamental set-up of a scanning microcell (shown with a free droplet): capillary, xyz-stage, video microscope, illumination.

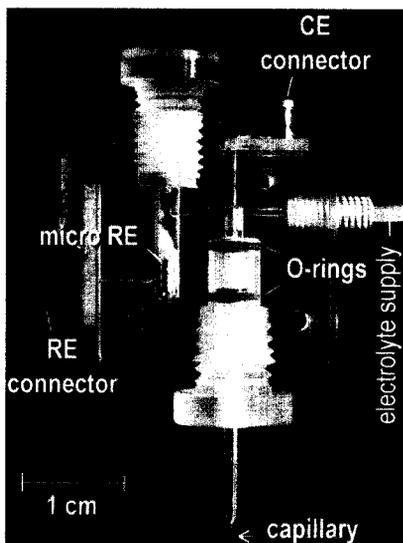


Fig. 2. Plexiglass carrier for capillaries with silicone rubber gaskets including reference and counter electrode.

channel diameter of $50 \mu\text{m}$. The size of the droplet can be varied by the electrolyte pressure, best results are obtained if the diameter of the droplet equals the outer capillary diameter at a capillary/specimen distance some $10 \mu\text{m}$. This arrangement is applicable to many electropolished metals which are usually non-wetting and allows scan across the surface.

Very rough or hydrophilic surfaces, however, must be investigated in a different way. *Silicone rubber gaskets* at the mouth of glass capillaries were introduced by a Swiss group.²²⁾ If the capillary is slightly pressed onto the investigated surface, the wetted area is a well reproducible and an evaporation of solvent becomes impossible. Capillary diameters down to $10 \mu\text{m}$ are possible. Hence, the wetted area on the samples can vary from 10^{-4} to 10^{-6}

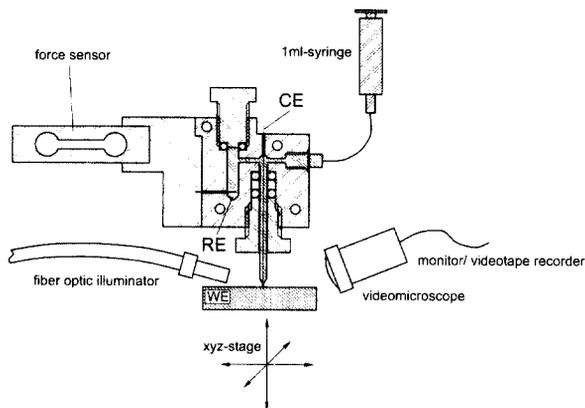


Fig. 3. Schematic set-up with capillary carrier, force sensor and monitoring.

cm^2 . A fast exchange of the capillaries is necessary, because glass capillaries tend to break and the silicone ring's life-time is limited. Therefore, a special *Plexiglass* carrier was developed (Fig. 2) which contains the micro reference electrode, the counter electrode, the electric connectors, and fittings for the electrolyte syringes.

The capillary carrier is combined with an xyz positioning system and a video microscope. The latter is used to control the droplet size and to identify structures on the investigated surface. A well defined working electrode area must be realized in subsequent experiments. If the silicone gasket is used a constant mechanical contact pressure must be applied to guarantee a reproducible wetted surface area. Therefore we added a strain gauge between carrier and xyz-stage (fig. 5). This sensor monitors the force between tip and sample and transfers it to the computer. In general, a perpendicular approach is necessary to guarantee a tight seal but a misalignment of up to 2° is acceptable due to the elastic properties of the silicone rubber.

Now any position on the sample can be addressed with high speed. A special computer algorithm guarantees a smooth touch of the surface. As a result, we can get surface images of all important parameters, which can be taken from cyclovoltammograms and other transient techniques or impedance spectra.

Besides local resolution the method of capillary based droplet cells has several advantages:

- The sample needs no preparation. Investigations can start immediately.
- Only the investigated surface is wetted. The other parts of the sample remain virgin.
- Hundreds of experiments become possible on one sample.

- The mechanical stress applied to the sample is small.
- The shape of the sample can be random. Only small areas with a diameter of some 10 μm must be flat.
- Only small amounts of electrolyte are needed.

The method was already applied to very many systems:

- Catalyst surfaces.²³⁾ The insulation of cutting edges or back-sides or the embedding of wires to get well defined surfaces, are examples for immobile masks fixed to the sample surface.
- Single crystals without embedding or other pretreatment, no mechanical stress.
- Single grains of polycrystalline material, like steel, Al, Ta, Nb, Hf, Zn and others.²⁴⁾
- Single micro particles.²⁵⁾
- Welding lines.

The droplet cells were not only used for a surface analysis but also for structuring of surfaces. With the droplet local modifications like passivation, metal or polymer deposition, etching etc. become possible.

4. Limits

Microelectrochemical investigations are usually limited by the resolution of current detection. A lower detection limit of 10 fA for low frequency current signals is typical for modern equipment. This means, cyclovoltammograms with typical current densities of some 10 $\mu\text{A}/\text{cm}^2$ are limited to electrode areas $> 1 \mu\text{m}$ in diameter. If experiments including higher frequencies are intended, e.g. impedance up to 1 MHz, the detection limit will be some 10 nA/cm². Accordingly, impedance measurements are limited to electrode areas with some 10 μm in diameter. This are rough estimates only and depend strongly on the special system under investigation. Experiments with the droplet cells are not limited by the capillary size (which can be as small as 100 nm) but by the detection limits of current. Other techniques with higher resolution avoid current detection (e.g. scanning reference electrodes) or need extremely high current densities, e.g. some 100 A/cm² in the case of SECM or much higher values at the tip of a STM (10⁴ to 10⁷ A/cm²).

As a result, the application of the droplet cell is limited to capillary diameters of about 10 μm , if the full range of experimental techniques with current densities down to $\mu\text{A}/\text{cm}^2$ is applied. This is, however, no problem, as many systems of interest (grains, micromechanics and microelectronics) belong to that range.

5. Summary

Electrochemistry started with a high normal (perpendicular to the surface) resolution in the range of nm, but the lateral resolution was bad (typically cm). In the mean time many microelectrochemical methods were introduced, usually by miniaturization of cell components but also by new concepts. Capillary-based droplet cells are a new and powerful concept for spatially resolved investigations. Capillaries with diameters of some μm position tiny electrolyte droplets (volume $< 1 \text{nl}$) on the sample. The wetted area (typically 10⁻⁴ to 10⁻⁶ cm²) forms the working electrode. The Scanning Droplet Cell can be used on wetting and non-wetting samples. Completely computer controlled surface scans became possible by the addition of a mechanical force sensor and enable us to record surface images of all common electrochemical parameter (currents, charge, peak potentials, resistances, capacities).

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