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M. M. Lohrengel · A. Moehring · M. Pilaski

Electrochemical surface analysis with the scanning droplet cell

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Abstract A new electrochemical device, the scanning droplet cell, is presented. Small electrolyte droplets are positioned on the sample surface and enable a spatially resolved surface analysis or modification. The droplet is simply held by its surface tension and, therefore, no surface pretreatment is necessary. According to the conventional 3-electrode arrangement all common potentiostatic and galvanostatic techniques, e.g. impedance spectroscopy, cyclic voltammetry, or current transients of potentiostatic steps, are possible.

1 Introduction

The miniaturization of electronic components, mechanical devices, or sensors demands the development of spatially resolved electrochemical techniques to analyze the structured surfaces. Some probe techniques show impressive resolutions (e.g. Scanning Tunnel Microscope STM, Electrochemical Microscope SECM) but lack the wide spectrum of the common macroscopic methods which are typically based on a potentiostatic set-up. Our intention was to apply the standard 3-electrode arrangement to small surface areas. No restrictions other than in a macro cell should be accepted, especially concerning:

- the composition of the electrolyte;
- the preparation of the sample;
- the experimental technique (potentiostatic or potentiodynamic, impedance);
- the electrical parameter of the cell (current densities up to A/cm^2, time constants of some µs).

Our concept was to reduce the wetted area of the sample. There are several strategies to do this:

- the use of (ultra-) microelectrodes [1, 2];
- immobile masks [3], sometimes prepared by laser modification of photo resists [4];
- mobile masks, e.g. produced by LIGA-technology [5];
- or probe techniques [6] like scanning microelectrodes [7, 8], especially the Scanning Electrochemical Microscope (SECM [9–13]), ion sensitive capillary electrodes [14]; the Scanning Tunnel Microscope (STM [15–17]); the Atomic Force Microscope (AFM [18]; the Kelvin probe [19–22]); focussed radiation (laser beams [23–25] or microellipsommetry [26–29]);

Newly developed concepts are capillary based microcells [30, 31] which will be presented here.

2 Capillary based droplet cells

An electrolyte droplet is dispensed and positioned on the surface by a capillary. The wetted circular area of the surface forms the working electrode (WE). The capillary contains reference (RE) and counter electrode (CE). The capillary can be made of different materials like metal (typically gold), glass, eventually covered with metal (gold), or plastic. Figure 1 shows concepts and ideas. The mouth diameter of the capillary differs from some 100 µm to some µm, dependent on the application. Two fundamental concepts are used to define the droplet diameter: free droplets and silicon rubber gaskets.

2.1 Free droplets

A free droplet can be formed between capillary and sample and is held by its own surface tension. This works if the capillary-sample distance is about 10–50 µm. The free droplet can be shifted across the sample, resulting in a "scanning droplet cell". The friction of the droplet is negligible and, thus, the sample must not bear any mechani-

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M. M. Lohrengel (✉) · A. Moehring · M. Pilaski
Institut für Physikalische Chemie und Elektrochemie,
Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1,
40225 Düsseldorf, Germany
e-mail: manuel.lohrengel@uni-duesseldorf.de

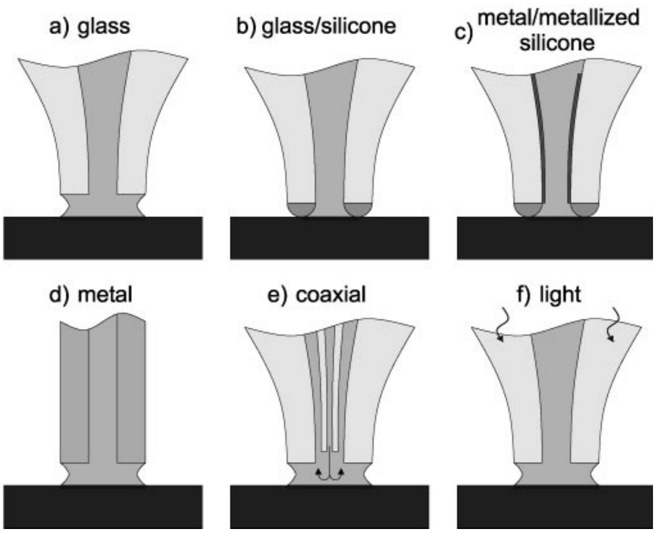

Fig. 1 a–f Concepts of capillary based droplet cells: Capillaries of glass (**a–c, e, f**) or metal (gold, **d**), free droplets (**a, d–f**) or capillaries with silicon rubber gaskets, coaxial flow-through concepts (**e**) and a version for photoelectrochemistry. The reference electrode is positioned at the upper end of the capillary. Counter electrode is a wire in the capillary channel or, if metal-coated (**c, d**), the capillary itself

cal stress. The free droplet requires non-wetting samples like most electropolished metals (contact angles close to 90°). This concept is used with gold capillaries or gold covered glass capillaries. The capillary acts as the counter electrode, the channel leads to the reference electrode. The cell resistance of this concept is very low (some mΩcm^2 due to the small WE/CE distance) and enables large current densities (up to 100 A/cm^2 for short times). The droplet diameter is given in a first approximation by the outer capillary diameter, but may, however, differ by some 10% due to oscillations of the droplet or variations of the contact angle. For precise experiments a calibration of the wetted area becomes necessary.

2.2 Capillaries with silicone gasket

The other principle uses a silicone rubber gasket formed at the mouth of the capillary [32]. The capillary is made of glass, the counter electrode is fixed in the capillary (wire or metal coverage of the inner capillary surface). The cell resistance is usually higher than in the case of free droplets. The capillary is slightly pressed against the sample so that the gasket defines the droplet volume. This enables the use on rough or hydrophilic surfaces. The droplet diameter is close to that of the capillary channel and is well reproducible. Once determined in a test experiment, the wetted area remains constant for many experiments. The pressure of the silicon gasket means some mechanical stress and thin films may delaminate in some cases.

3 Experimental set-up

Figure 2 shows how the capillaries are fixed to an acryl glass carrier. The capillary is held and tightened by O-rings. The carrier contains the micro reference electrode and is equipped with special fittings for syringes. Stepper motor operated mL- and µL-syringes are used for dosing and rinsing. The whole carrier is positioned above the sample by an XYZ-stage. Sample surface and droplet size are monitored by a video microscope. This cell design allows the application of all the common electrochemical techniques in a wide range: impedance spectroscopy (frequencies

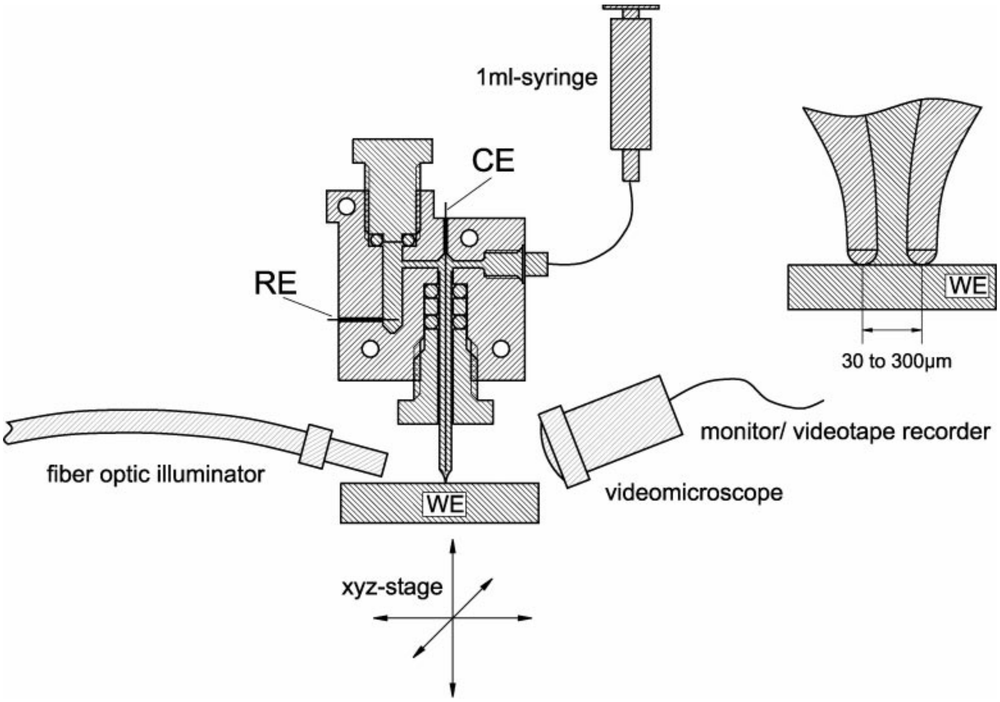

Fig. 2 Typical set-up: acryl glass carrier for capillaries with syringes, micro reference electrode, fixed to an XYZ-stage. Illumination and monitoring with a video microscope

1 mHz < f < 1 MHz), cyclovoltammetry (sweep rates up to 1000 V/s), or current transients of potentiostatic steps (times 1 µs < t < 1000 s, current densities 100 nA/cm^2 < i < 100 A/cm^2) [2].

Measurements can be carried out in different ways. In the scanning mode, the droplet is slowly shifted across the surface. It remains stable but shows some slight oscillations in size and, thus, a variation of the wetted area of about 20% exists. Therefore, this technique is only suitable if large variations of the local electrical parameter exist. For precise experiments it is necessary to use stop-and-go techniques, namely shifting the droplet to the first position, stopping, taking the local data, and shifting to a new position, and so on. This technique means a possible accumulation of contaminations. Better is the technique of the "hopping droplet", that is, the capillary after each experiment is lifted and rinsed before a new position is addressed.

4 Applications

The scanning droplet is applicable to various technical surfaces, typical examples are shown in Fig. 3. A spatially resolved analysis or local modification of metal surfaces (sheets, rods, inner surface of tubes, die cast housings), structured surfaces (single grains of polycrystalline materials, local corrosion, microelectrodes and -arrays, technical electrodes, single crystals, solder or contact pads of printed circuit boards, structured silicon wafers) becomes possible.

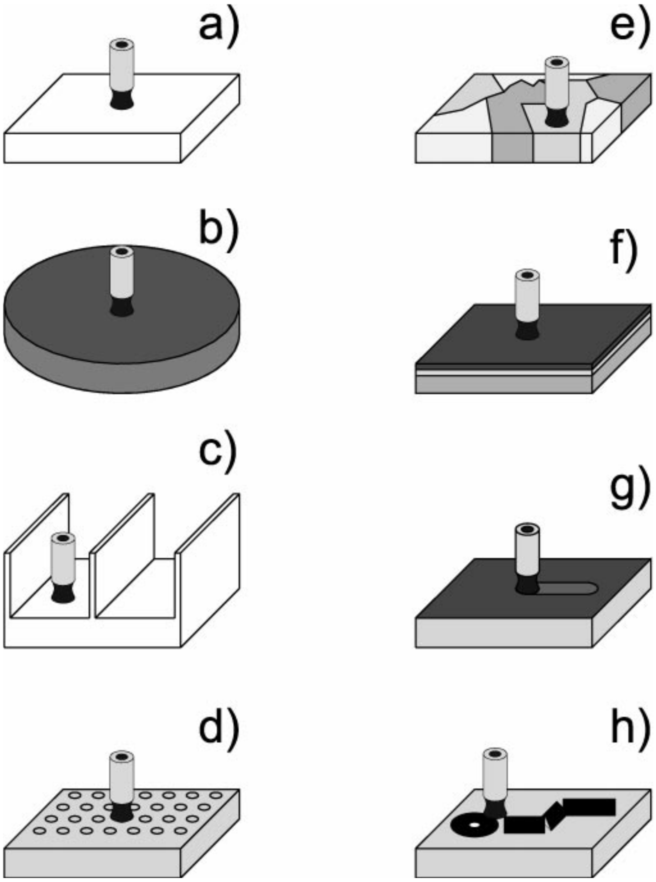

Fig. 3 Typical applications of droplet cells: (**a**) local investigation of technical surfaces without proparation; (**b**) investigation of wafers or single crystals; or (**c**) of metal parts of complex shape; (**d**) addressing of microelectrodes; (**e**) investigation of single grains of polycrystalline material; (**f**) preparation or analysis of thin film sandwiches without mechanical stress; (**g**) local galvanization or modification or (**h**) surface analysis of contact or solder pads

4.1 Oxide layers

Figure 4 shows the surface of a typical sample, in this case polycrystalline Zr. The sample was first of all strongly electropolished (lower part) and then partially anodized to 10 V (upper part). The oxide film formed by this procedure becomes visible due to light interference, the color is yellow to brown, depending on the film thickness. As the thickness depends on the crystallographic orientation of the metal, the grains become visible due to the different oxide thicknesses. The sample in Fig. 4 is a large grain material and enables easy addressing and investigation of different grains [33].

The interference colors of oxide films (e.g. on Ta, Nb, Ti, Zr) enable an elegant method to determine the exact size of the wetted area. After the experiment the sample is anodized to a high value and the resulting colored spot is recorded with the video microscope and measured by image processing [33].

Figure 5 shows the potentiodynamic growth of oxide films on different grains on Al. Usually, an oxide growth independent of the substrate orientation is assumed. In fact, the current densities are very similar. This means equal charge consumption and, therefore, equal amounts of oxide. The onset of current at slightly different potentials can be due to different roughnesses of the grains surfaces and, hence, to different initial thicknesses. More interesting are the differences in capacity, though the charges are equal. Obviously, the densities and/or the dielectric permittivities of the oxide films are grain dependent.

A consequent investigation of grain dependent oxide growth becomes complex as many experiments are necessary:

- record of a crystallographic image of the sample, e.g. by electron back scattering diffraction (ESBD);
- electrochemical image, i.e. current densities, charges and capacities on different grains;
- microellipsometric determination of the film thickness;
- topographic and optical image to guarantee a defect-free surface (no corrosion pits etc.).

From this reliable parameters like oxide formation factors, thicknesses, densities, and dielectric permittivities for different grains can be obtained. Such investigations are in progress.

4.2 Optical sensors

Another interesting aspect of the droplet cell technique is structuring of thin film devices. An example is given in

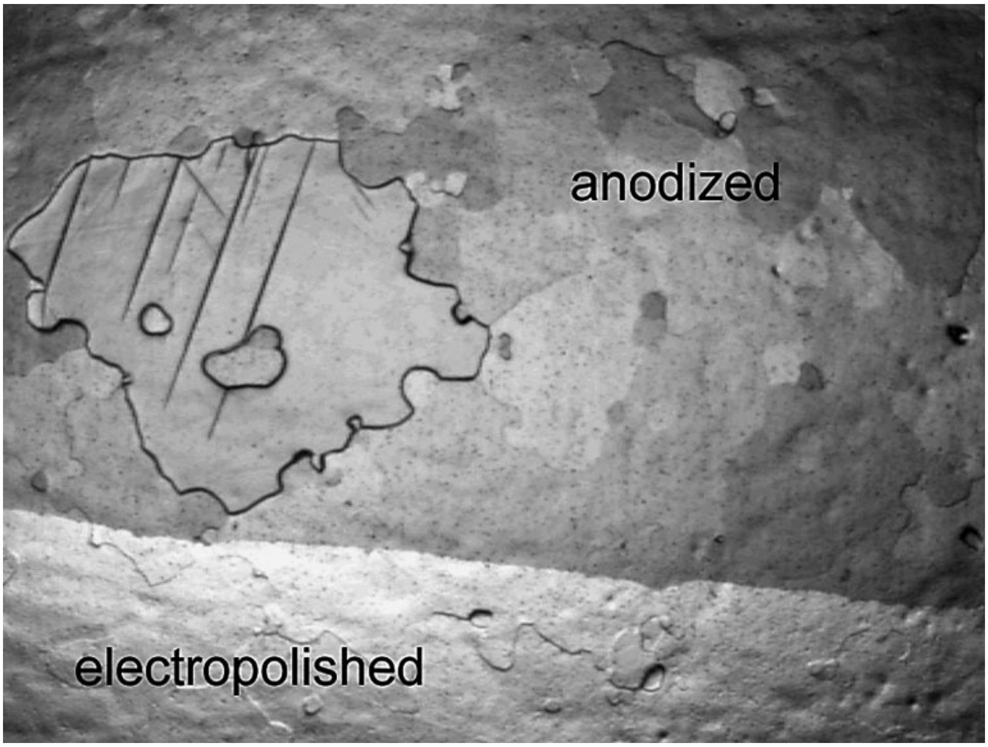

Fig. 4 Surface of a large grain Zr sample, strongly electropolished (*lower part*). The *upper part* was then anodized to 10 V. the grain structure of the polycrystalline material becomes visible

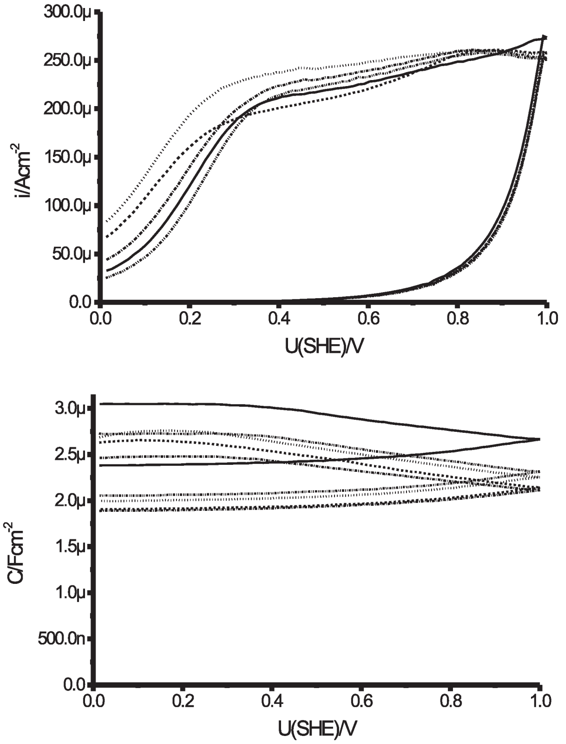

Fig. 5 Potential-current curves of anodic oxide formation on different grains of Al at 25 °C, pH = 6 (*top*) and corresponding capacities (*bottom*)

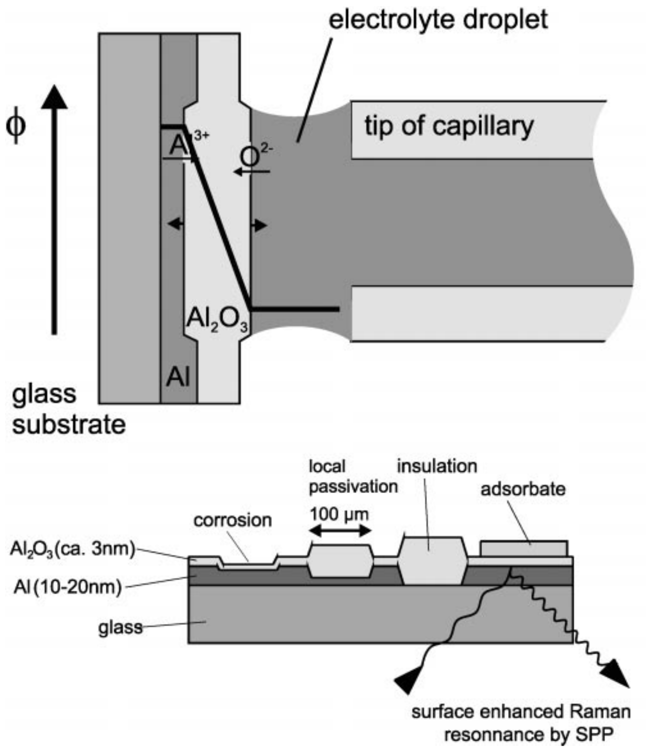

Fig. 6 Schematic view of the optical sensor and preparation with the scanning droplet cell: formation of well defined oxide films and insulating (completely oxidized) areas in a 20 nm Al film on glass

Fig. 6. Transparent carriers, e.g. thin glass panes, are vapor deposited with Al thin films of 10 to 20 nm. After preparation the Al film is usually covered by a native oxide film of some nm. This film is a dense, corrosion resistant, insulating barrier and can be electrochemically varied from 1 to some 100 nm. If the oxide surface is

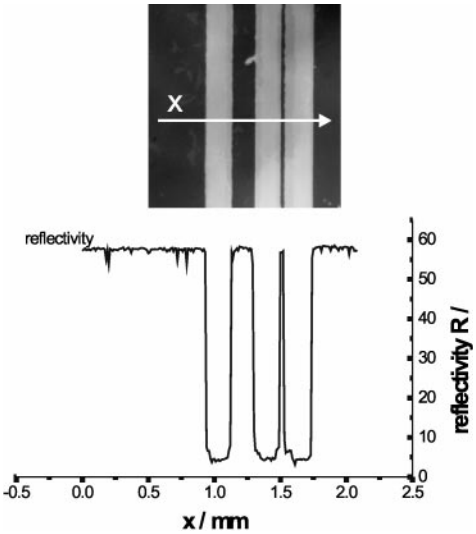

Fig. 7 Lines of complete oxidation of the Al film, written with a free droplet (*top*), and analysis by scans of reflectivity (laser profilometry, *bottom*)

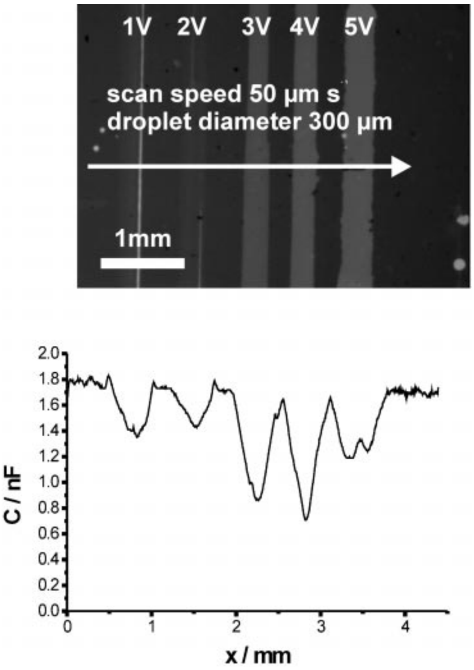

Fig. 8 Lines of anodization written with a free droplet at different potentials (*top*)and crosswise capacity scan for analysis (*bottom*)

exposed to an electrolyte, solved molecules can adsorb (Fig. 6). Illumination of the glass side can stimulate surface plasmon polaritons at the interface Al/oxide which interact with the adsorbed molecules. Result is an enhanced Raman scattering [34–36].

Such an optical sensor requires a thin, dense, inert oxide film (<5 nm), a thin metal film (Al) and a transparent substrate, e.g. glass (Fig. 6). The Al surface must be structured in two ways. Parts of the Al must be completely oxidized to form insulating areas, similar to a printed circuit board in electronics. Other parts must be covered with homogeneous, well defined oxide film of known thickness as described above.

Figure 7 shows in upper part a photo micrograph of three insulating lines of about 200 µm written at 20 V with the scanning droplet. They were analyzed by their reflectivity with a laser profilometer (bottom). The crosswise scan shows the sharp boundaries of the lines.

Figure 8 shows oxidation scans at different potentials in the range 1 to 5 V. Under these conditions the metal is only partially oxidized, resulting in oxide film thicknesses from 4.2 nm (1 V) to 10.6 nm (5 V). We carried out a continuous impedance scan (single frequency 1023 Hz) with the scanning droplet cell. The resolution is less satisfying than in Fig. 7, because the probe has the same diameter as the structure. Nevertheless, decreasing capacity with increasing thickness can be observed.

5 Conclusions

Capillary based droplet cells are a valuable tool for spatially resolved investigations of conducting surfaces. Capillary diameters from some µm to some 100 µm are used and determine the resolution. This resolution is worse than that of some special probe techniques (e.g. STM); the 3-electrode arrangement which is used, however, allows the full range of common electrochemical techniques. This enables a surface analysis as well as preparation and structuring (galvanization, passivation, deposition) of thin film devices.

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