Determination of the shape and dimensions of a meniscus under stress for pipette based electrochemical microscopies

Nathan Goffart,[a] Jon Ustarroz,[a] and Thomas Doneux[a]

[a] *Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculté des Sciences, Université libre de Bruxelles (ULB)*

Boulevard du Triomphe, 2, CP 255, B-1050 Brussels Belgium

Nathan.Goffart@ulb.be

Scanning electrochemical cell microscopy (SECCM) and other local electrochemical probe microscopies based on (nano)pipettes enable the simultaneous acquisition of topography and local electrochemical reactivity. As such, they have been successfully employed to study many electrochemical reactions at the nanoscale[1]. This is possible due to the confinement of the reaction cell in the meniscus formed between the nanopipette and the substrate. To drive the electrochemical reactions, a potential is applied between a quasi-reference counter electrode (QRCE) and the substrate which acts as the working electrode (WE). A schematic is shown in Figure 1.

The electrochemical response is directly dependent on the exact shape and dimensions of the meniscus, i.e. on the pipette inner and outer diameter, pipette-substrate distance, meniscus footprint on the substrate, etc. Most often, to interpret the experimental data, experimenters must rely on assumptions and numerical simulations to assess the approximate shape of the meniscus.

In the present work, we have implemented confocal fluorescence microscopy as an efficient methodology to determine the dimensions of a meniscus. The method consists in using a fluorescent dye dissolved in solution and to reconstruct in 3D the shape of the meniscus from a series of 2D fluorescence images recorded at different heights of the meniscus (a so called "z-stack")[2].

In this work, we use a custom-made semitransparent gold substrate as working electrode. In the aim of modifying the wettability of the surface, we used self-assembled monolayers (SAMs). A large choice of thiolated molecules allows us making the surfaces more hydrophilic or hydrophobic.

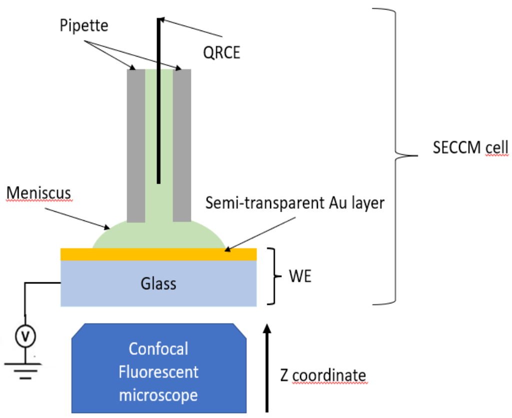

Figure 1 Representation of the experimental setup, SECCM and confocal microscopy

We compress or stretch the meniscus in the *z*-coordinate and evaluate how the shape of the meniscus is affected by the movement and resist to the stress. Different pipette diameters below 100 µm have been investigated and compared to the SECCM (electrochemical response) and SEM (footprint view) results.

This work allowed a direct determination of the exact meniscus shape for electroanalytical methods, in the micro scale. As such, it provides a better understanding of the voltammetric responses measured in SECCM.

References

(1) Bentley, C. L.; Kang, M.; Unwin, P. R. Nanoscale Surface Structure–Activity in Electrochemistry and Electrocatalysis. *J. Am. Chem. Soc.* **2019**, *141* (6), 2179–2193.

(2) Bouffier, L.; Doneux, T. Coupling Electrochemistry with in Situ Fluorescence (Confocal) Microscopy. *Curr. Opin. Electrochem.* **2017**, *6* (1), 31–37.