Keysight Technologies
Introduction to SECM and Combined AFM-SECM

Application Note

Introduction

Scanning electrochemical microscopy (SECM) is a powerful scanning probe technique, which is suitable for investigating surface reactivity, and processes at the solid/liquid as well as liquid/liquid interface. Redox reactions and their kinetics involving active species are of fundamental importance in emerging research and application areas ranging from the analysis of biochemical signaling processes e.g., at live cells and tissues to relevant questions in material sciences including e.g., fuel cell technology, catalysis, sensing, and environmental chemistry.

While electrochemical scanning tunneling microscopy (EC-STM) and electrochemical atomic force microscopy (EC-AFM) are predominantly based on imaging structural/ topographical and electronic changes at a biased macroscopic sample surfaces, SECM advantageously combines fundamental microelectrochemical information via the entire palette of electroanalytical techniques with imaging modalities. The scanning electro-chemical microscope was introduced by Bard and coworkers with the fundamental prin-ciple entailing scanning a biased ultra-microelectrode (UME) as an imaging probe across the sample surface, while recording Faradaic (redox) currents at the UME, and optionally, also at the sample.[1] In contrast to EC-AFM and EC-STM, SECM is not limited to conduc-tive or biased samples. In addition, due to thoroughly developed theoretical descriptions and models SECM readily allows the quantification and prediction of experimental data. Since the introduction of SECM, a multitude of imaging modalities have been developed and experimentally demonstrated based on a wide variety of electrochemical analysis techniques including DC voltammetry[2], redox competition mode[3], and alternating current (AC)-SECM imaging[4].

The *so-called* feedback mode is the most commonly applied imaging mode in SECM[5]. Here, the probe and the sample are immersed in a solution containing a redox active species (e.g., R providing a reversible redox behavior governed by diffusion). If an appro-priate potential is applied at the probe, R is oxidized to O, thereby resulting in a steady state Faradaic current, which is proportional to the radius, r of the UME and the concen-tration, c of the redox species following I = 4nFDcr (n = number of transferred electrons, F = Faraday constant, D diffusion constant of the redox active species).

If now the biased probe (i.e., the UME) is moved toward a sample surface (Figure 1) at a distance of several electrode radii, the faradaic current measured at the probe is increasingly affected by the sample surface properties. An insulating sample surface or surface feature leads to a diffusion limitation of electroactive species (here, R) towards the electrode, and hence, results in a reduced faradaic current vs. the steady state current (Figure 1 left). A conductive sample surface or surface feature results in a locally increased concentration of the redox species, as the oxidized species can be regenerated at the sample surface (here by reduction), which leads to an instantaneously increased faradaic current (Figure 1 right) in comparison to the steady state current.
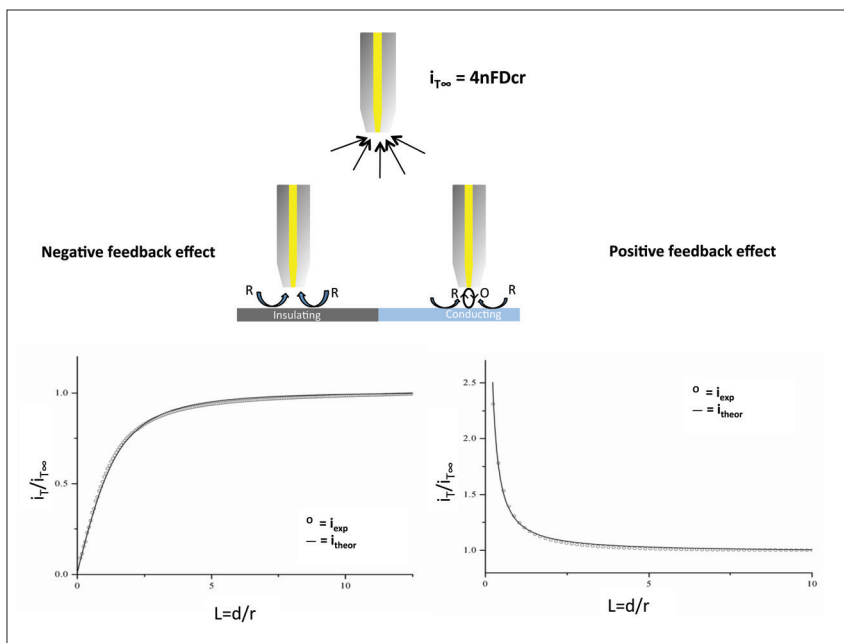

Figure 1. Feedback mode. Left: negative feedback effect due to hindered diffusion of the redox active species towards the UME. Right: positive feedback effect due to the regeneration of the redox media-tor at the sample surface.
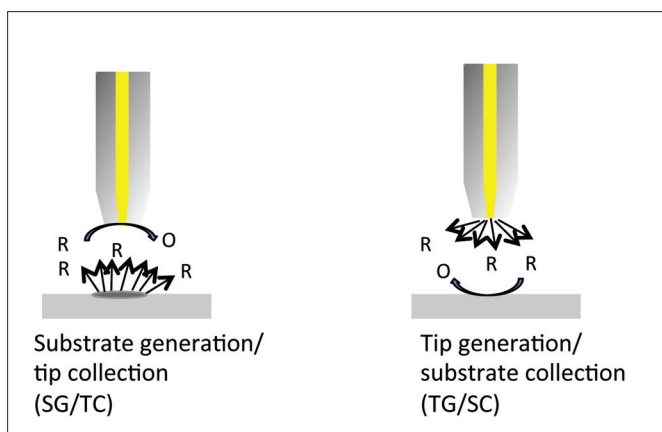
Figure 2. Generation collection mode. Left: substrate generation/tip collection mode. Right: tip generation/substrate collection mode .

The generation/collection mode (Figure 2)[6] is based on detecting electro-active species at the UME, which are generated at the substrate surface *(substrate generation/tip collection mode SG/TC, Figure 2 left)*. This mode has been used for imaging transport phenomena through membranes, investigation of corrosion processes and imaging of biological samples such as immobilized enzymes. *Tip generation/substrate collection mode (TG/SC mode, Figure 2 right)* is based on the generation of an electroactive species at the UME, which is detected at macroscopic electrode surface. This mode is mainly applied for time to flight experiments in order to study fast homogeneous reactions.

The following schemes present the principle of feedback mode (Figure 1) and generator collector mode (Figure 2):

Applications of SECM

SECM has evolved from an expert tool into a versatile scanning probe technique, which is reflected in a steadily increasing number of applications. As SECM is extremely versatile for investigating dynamic surface processes and is not limited to certain sample types or sizes, SECM has been applied to:

Investigation of homogeneous and heterogeneous electron transfer reactions

Imaging of biologically active processes

– Live cell monitoring
– Respiratory activity
– Analysis of membrane transport
– Enzyme activity
– Monitoring release and uptake of signaling molecules

Surface modification

– Redox etching
– Metal or polymer deposition
– Patterning of self-assembled monolayers

Analysis of thin films (e.g., pinhole detection, conformity, etc.)

Screening of catalytic material (e.g., fuel cell catalysts)

Corrosion processes

– Triggering and localized monitoring of corrosion processes
– Detection of precursor sites for e.g., pit corrosion
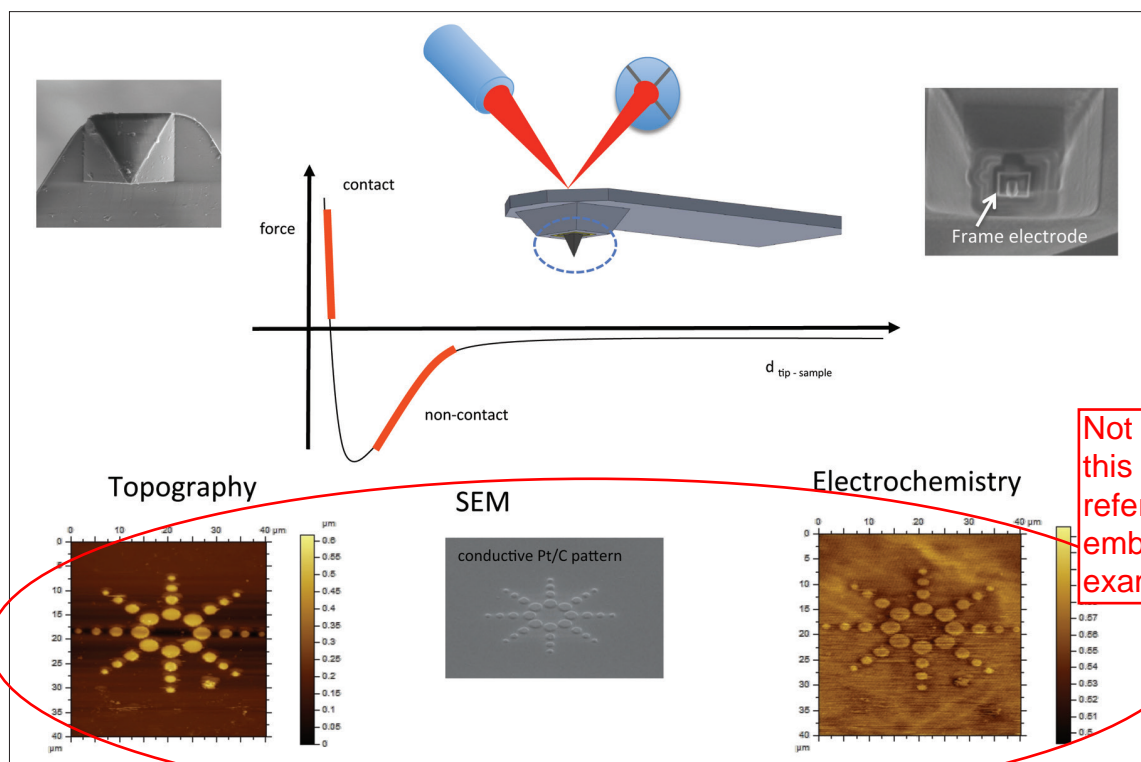– Biocorrosion

Figure 3. Combined AFM-SECM measurements based on AFM tip-integrated electrodes. Bottom: Simultaneously recorded images showing the topography (left) of the Agilent logo deposited from platinum/carbon composite by an ion beam-induced deposition (SEM image, middle) and the electrochemical image recorded in feedback mode SECM (right).

A drawback of conventional SECM compared to AFM and STM is the limited resolution, which results from the current-dependent positioning of the UME in close proximity to the sample surface and imaging in a constant height regime. As the required imaging distance is directly correlated to the UME radius, most SECM experiments are performed using micrometer-sized UMEs for avoiding probe crashes and potential convolution of surface roughness with electrochemical information, which may lead to misinterpretation of the obtained electrochemical data. While nanoelectrodes are reported in literature, their usage in conventional SECM experiments for reliable imaging remains challenging. Integrating the SECM functionality into AFM (see Figure 3) enables high-resolution topographical imaging while simultaneously mapping electrochemical information via an AFM tip-integrated electrode. Basically two approaches have been developed within the last years; bifunctional probes with the electroactive area at the tip apex and micro-fabricated probes with a non-conductive AFM tip and a frame or ring electrode located below the tip.[7] Using AFM-SECM probes, inherently synchronized structure–activity information is uniquely provided. In particular, in biomedical research, in materials science (e.g., corrosion studies), and energy research (e.g., fuel cells and batteries) essential interest is geared towards analyzing multiple parameters in correlated measurements on continuously changing samples/surfaces.

Produced via microfabrication techniques[8], these bifunctional probes ensure a constant and deliberately selected distance between the tip-integrated electrode, which is located recessed from the insulating AFM tip, and the sample surface. As the electrochemically active electrode area is separated from the insulating tip, the electrode is advantageously not in direct contact with the sample surface and hence, does not require scanning the sample twice (e.g. for a biased sample).[9] In addition, having such a recessed electrode, the electrode surface may be easily modified with electrocatalytic layers or conductive polymers[10]. Chemical modification of the electrode surface with biorecognition architectures (e.g., immobilized enzymes, antibodies, etc.) results in tip-integrated electrochemical (bio) sensors[11] harnessing enhanced molecular recognition with high selectivity, and specificity. In addition, different electrode materials such as boron-doped diamond, which is characterized by a large potential window, chemical inertness, and low background currents, can be integrated into the AFM tip[12].

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