

## Scanning Electrochemical Microscopy - SECM

The probe of a Scanning Electrochemical Microscope (SECM) scans the sample surface at a distance in the range of the tip diameter (0,1-50 $\mu\text{m}$ ). Meanwhile it measures the current (down to 100pA) emerging from a redox reaction taking place at the tip. At such small distances the signal depends on the reacting species generated at the sample surface. By wisely choosing a specific redox reaction, different information can be obtained. Like this conducting and non-conducting surfaces can be differentiated, topography measurements can be performed, anodic and cathodic sites of a corroding sample can be detected, the surface composition can be analyzed, and so on. Therefore the SECM operates in different modes:

### Negative feedback mode

This mode is the simplest mode. The reduction current depends on the tip to sample distance. The sample is an insulator and hinders the diffusion of the electro-active species. (cf. Fig. 2) So the detection of insulating and conducting areas as well as topography scans can be performed.

### Redox competition mode

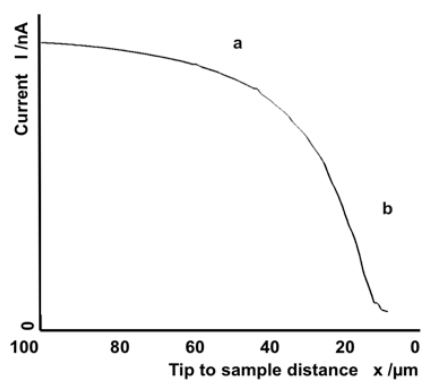
Tip and sample compete for the same electro-active species. Areas on the sample of higher activity reduce the current measured at the tip.

### Tip-generation and sample-collection mode

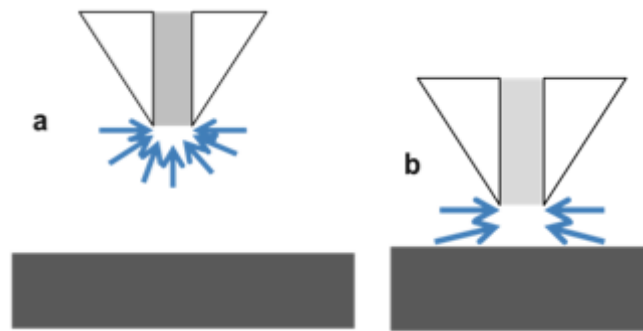
On the tip e.g. water is oxidized to oxygen. The signal measured arises from the O<sub>2</sub> reduction at the substrate.

### Tip-collection and sample-generation mode

In this mode the substrate must be polarized in order to reduce oxygen. Thereby H<sub>2</sub>O<sub>2</sub> is generated as a by-product. The signal collected at the tip is the oxidation current of peroxide.



*The current depends on tip to sample distance: Tip is a) far away b) and close to sample surface.*



*Working principle of a SECM. Current is limited at small tip to surface distance. a) if the tip is far away from the surface there is no local restriction for electroactive species. The current is diffusion limited. b) Near the surface of an insulator the current depends on the tip-to sample distance.*