Introduction to ac-SECM

06/12/13

N. Murer, Ph. D.
Scanning probe systems specialist
nicolas.murer@bio-logic.net

Objectives

Provide a better understanding of

1. What the ac-SECM technique is
2. Which information can be obtained
3. What the advantage of ac-SECM over dc-SECM is

Outline

1. Prerequisite : dc-SECM
2. ac-SECM principles
3. Applications
4. Data

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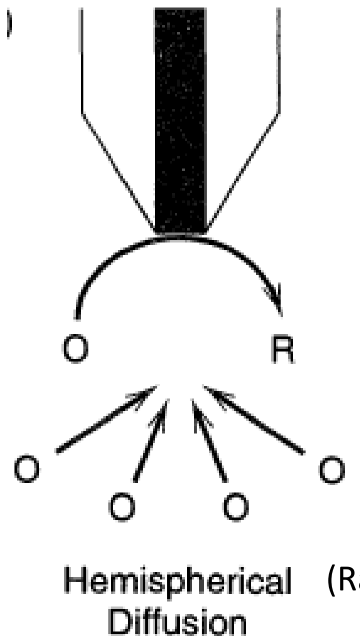
UME in bulk solution

UME : Ultra MicroElectrode

Definition : « At present, there is no broadly accepted definition of a UME, although there is a general agreement on the essential concept, which is that the electrode is smaller than the scale of the diffusion layer developed in readily achievable experiments.[1] »

Steady-state response of a disk UME to a Large-Amplitude Potential Step



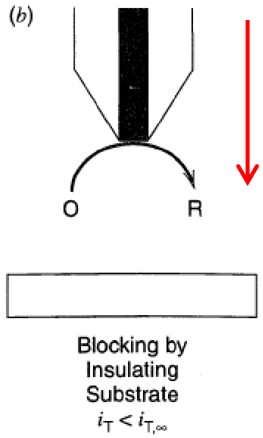
(Radial and normal)

$$i_{T,\infty} = 4nFD_OC_O^*a$$

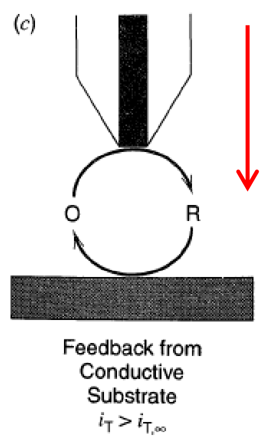
1. A.J. Bard, L. R. Faulkner, Electrochemical Methods, 2nd edition, Wiley & Sons, NYC

Feedback mode : approach curves

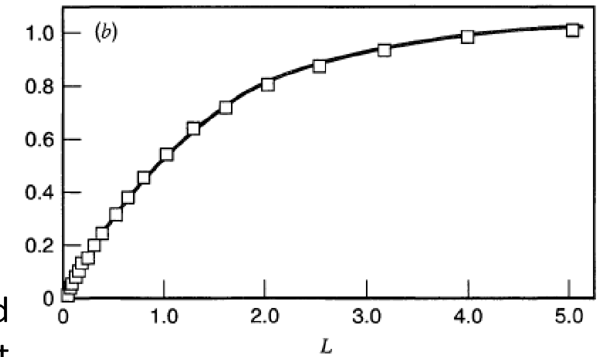
Negative feedback

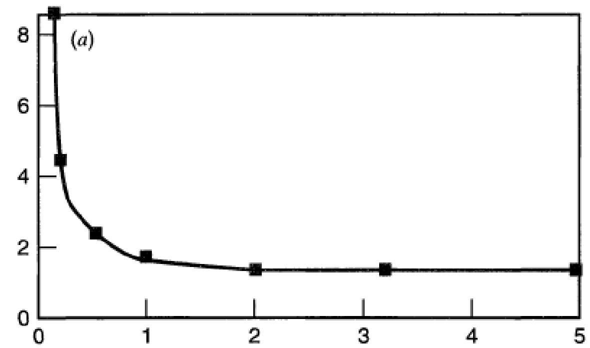


Positive feedback



Normalized tip current $i_T/i_{T,\infty}$



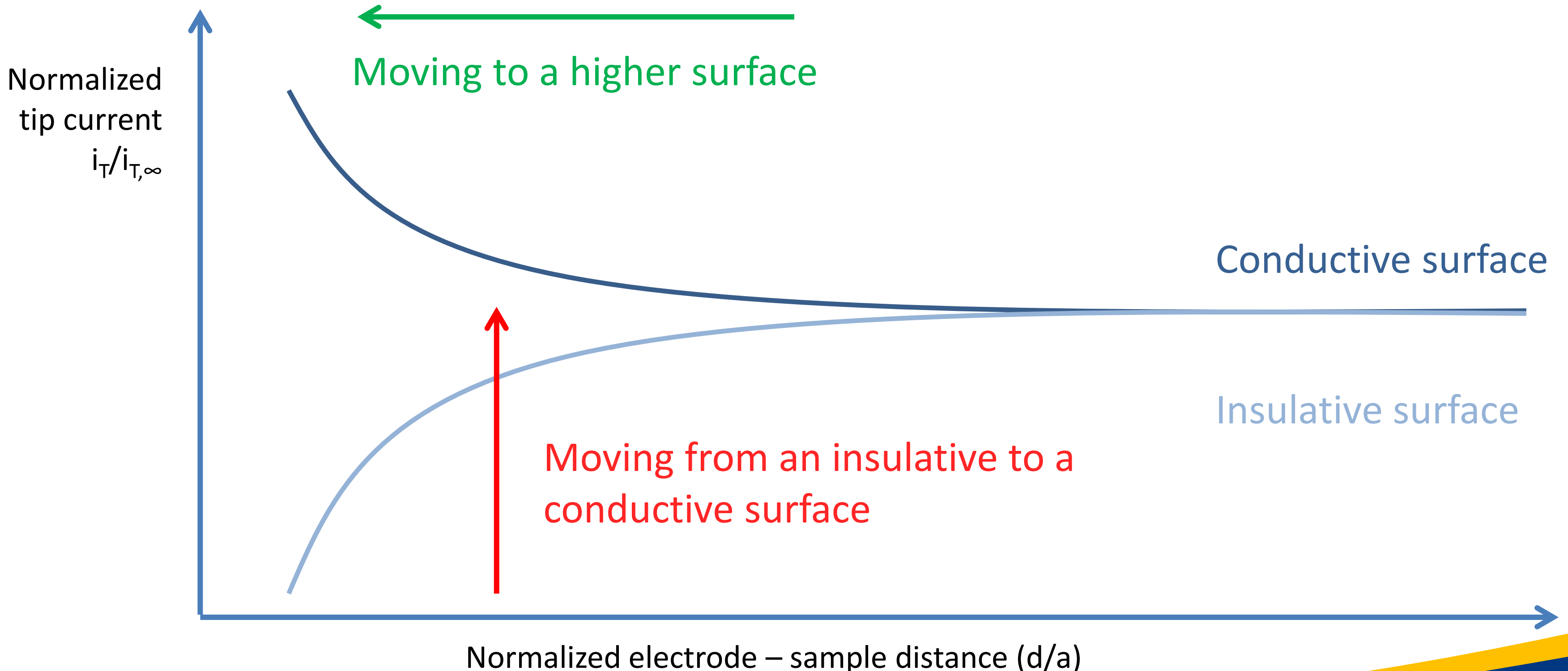


Normalized electrode – sample distance (d/a)

1. A.J. Bard, L. R. Faulkner, Electrochemical Methods, 2nd edition, Wiley & Sons, NYC

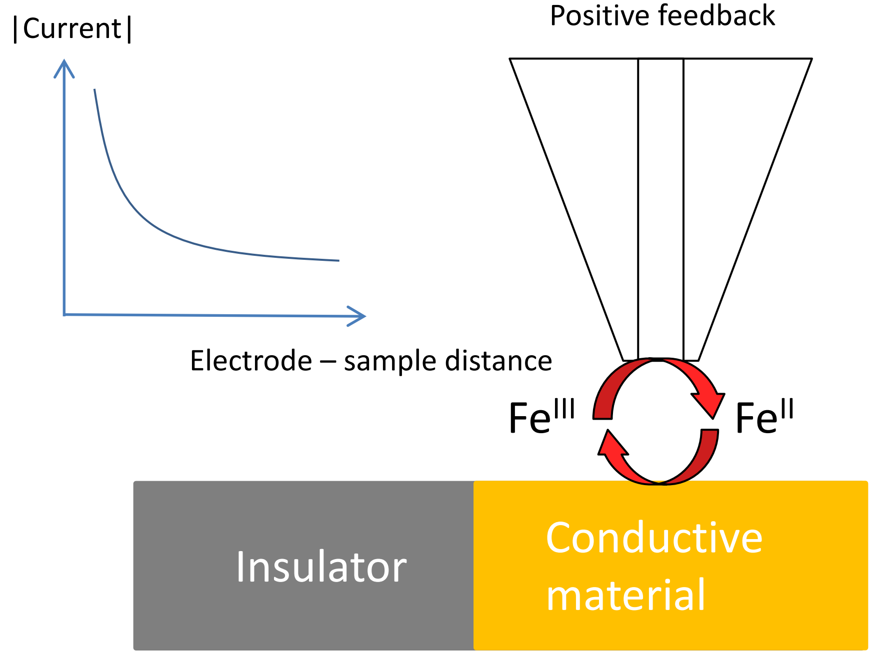
Feedback mode : approach curves

As the probe is sufficiently close to the surface, the current changes if :
. the conductivity of the surface changes
. the topography of the surface changes



Limit in SECM

1. The use of a redox mediator



SECM requires the use of an electroactive species : $FeCN_6^{3-}$, $Ru(NH_3)_6^{3+}$, which can interact with either the substrate for instance dissolved metal ions from corrosion or with the other species contained in the electrolyte *i.e.* corrosion inhibitors.

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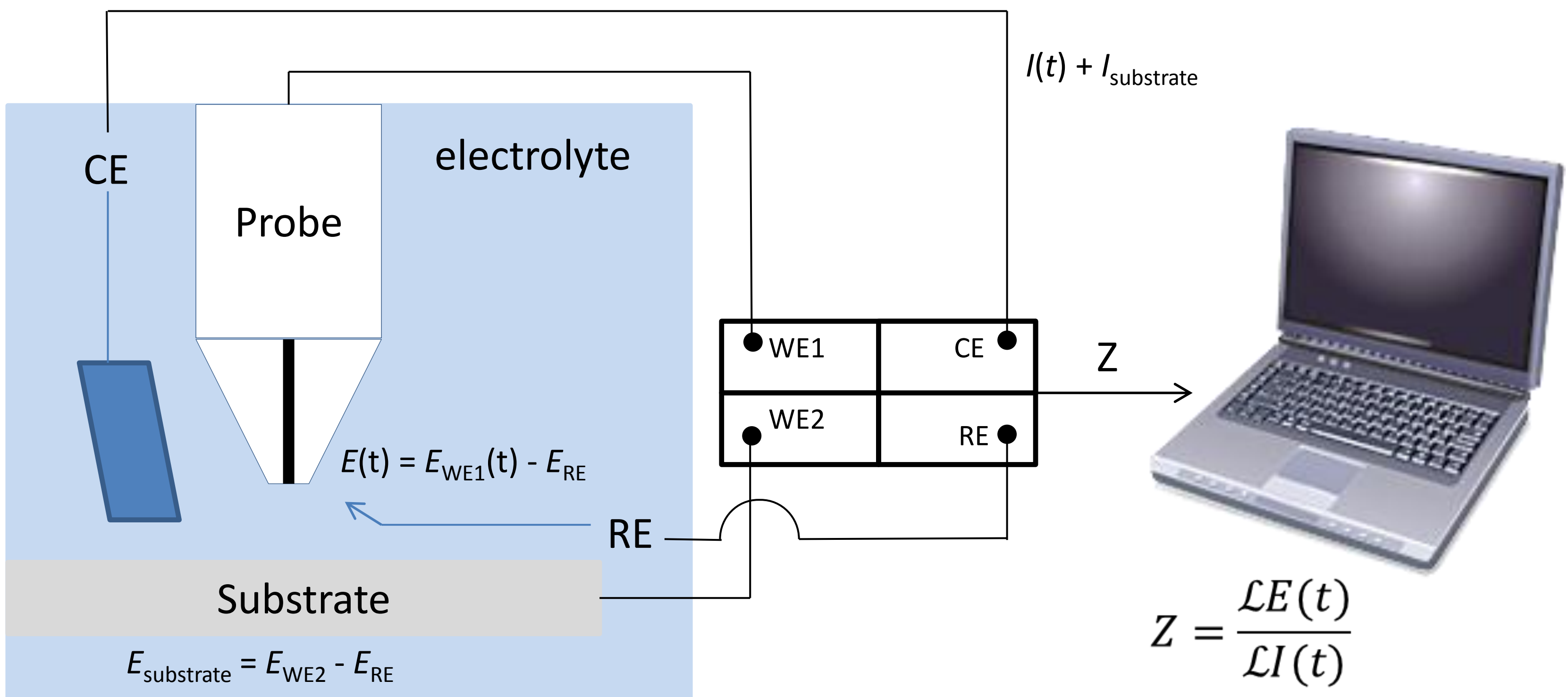
ac-SECM set-up

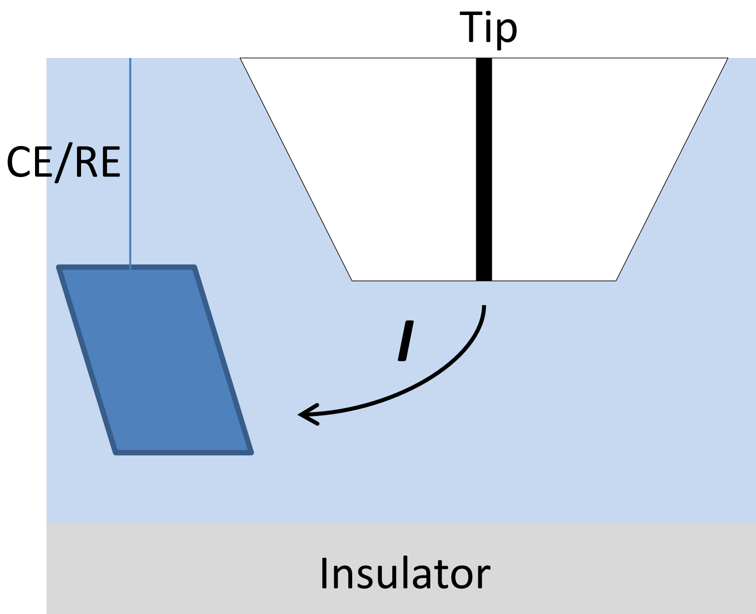
ac-SECM is performed by adding a sinusoidal voltage bias to the dc voltage applied to the tip. The current response is recorded to provide the complex value of the impedance.



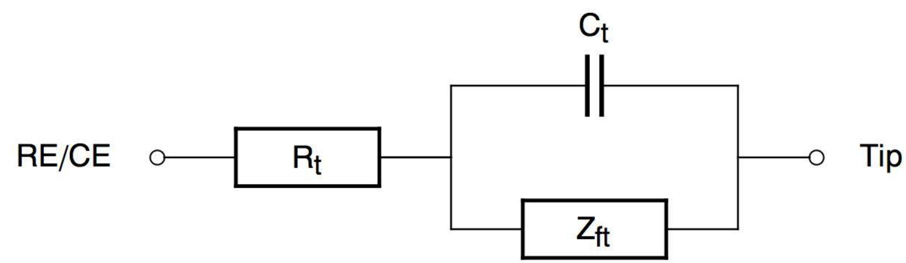
$$Z = \frac{\mathcal{L}E(t)}{\mathcal{L}I(t)}$$

The electrochemical cell, comprised of the solution between the tip of the probe and the substrate, can be modelled using equivalent circuits.
The equivalent circuits depend on the type of the substrate.

ac-SECM measurement on an insulating substrate



Equivalent electrical circuit (the impedance of the CE is neglected) :

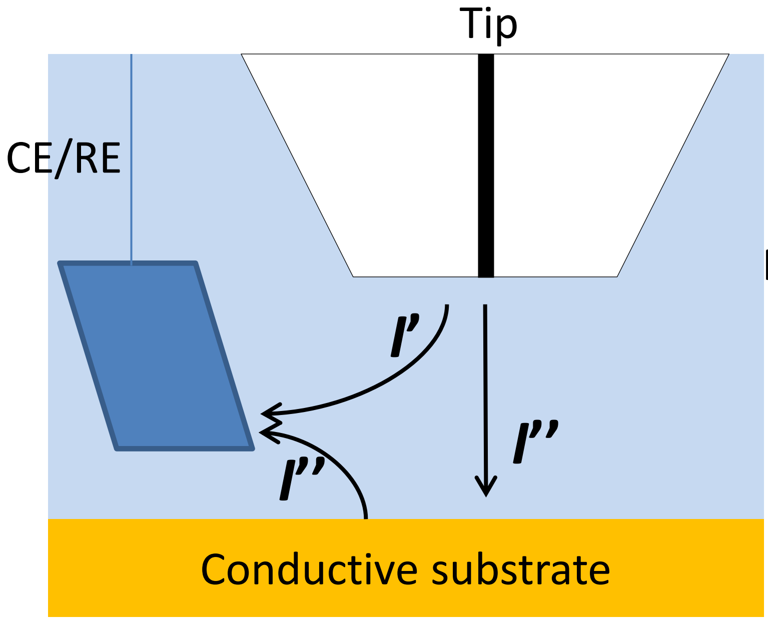


Z_{ft}: faradaic impedance of the tip
C_t: double layer capacitance of the tip
R_t: solution resistance between the tip and the reference electrode

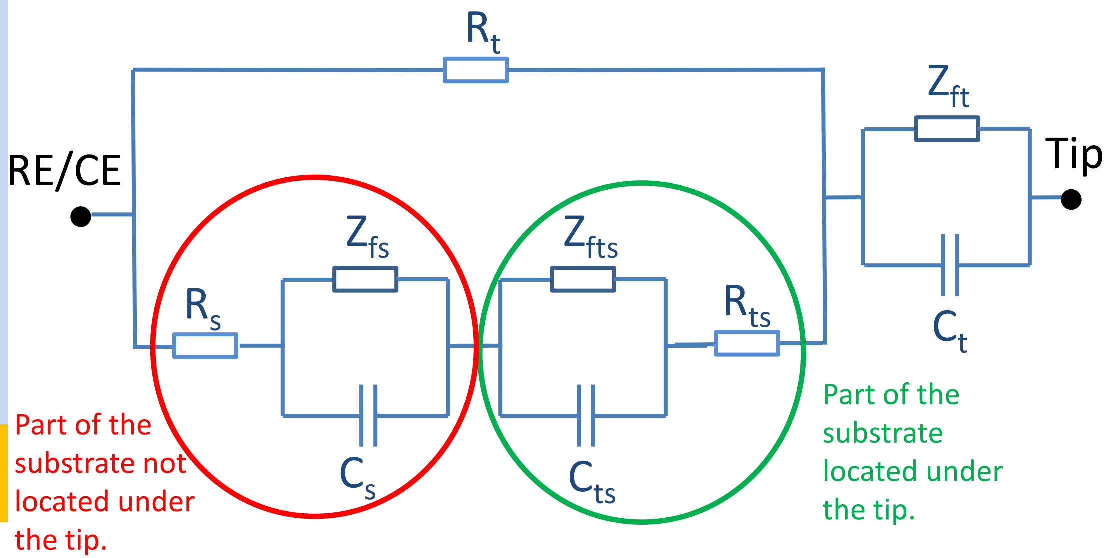
All the ionic current flows through the solution between the CE and the tip. As the tip approaches the insulative surface, R_t increases (due to the blocking of the diffusion) and becomes dominant w.r.t. Z_{ft} and C_t.

Taken from :
2. A.S. Baranski, P. M. Diakowski, J. Solid State Electrochem., 8 2004 683-692
3. P.M. Diakowski, A.S. Baranski, Electrochim. Acta, 52 2006 854-862

ac-SECM measurement on a conductive substrate



Equivalent electrical circuit :

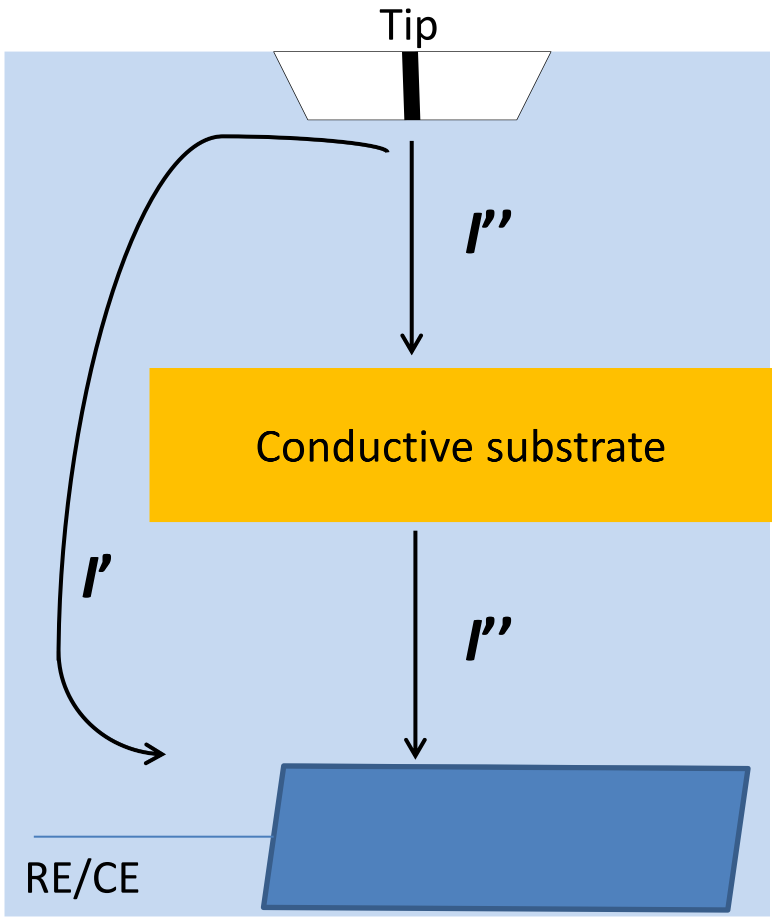


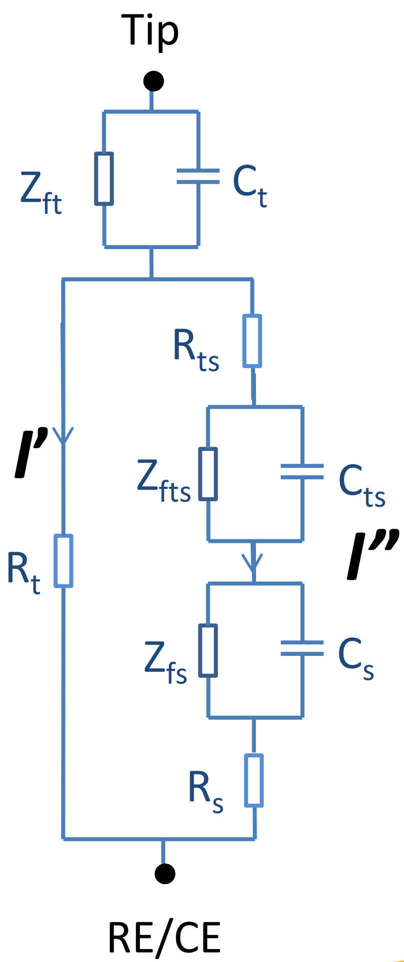
Now the current has two paths: either directly through the solution (I') or through the conductive substrate by crossing the substrate/electrolyte interface twice (I'').

Z_{ft}: faradaic impedance of the tip
C_t: double layer capacitance of the tip
R_t: solution resistance between the tip and the reference electrode
Z_{fts}: faradaic impedance of the part of the substrate covered by the tip
C_{ts}: double layer capacitance of the part of the substrate covered by the tip
R_{ts}: solution resistance between the tip and the substrate
Z_{fs}: faradaic impedance of the part of the substrate not covered by the tip
C_s: double layer capacitance of the part of the substrate not covered by the tip
R_s: solution resistance between the substrate and the reference

ac-SECM measurement on a conductive substrate

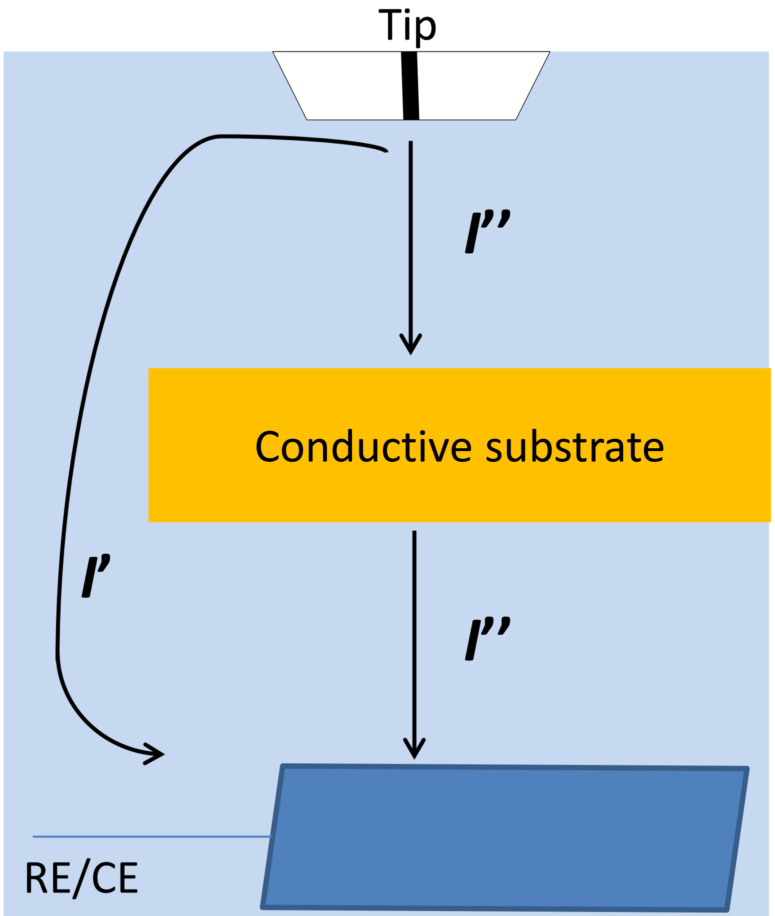
This cell geometry is equivalent to the preceding one.

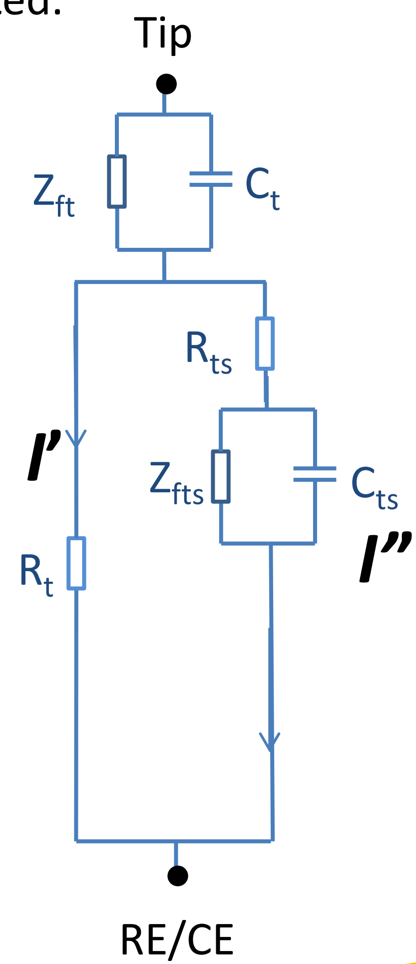




ac-SECM measurement on a conductive substrate

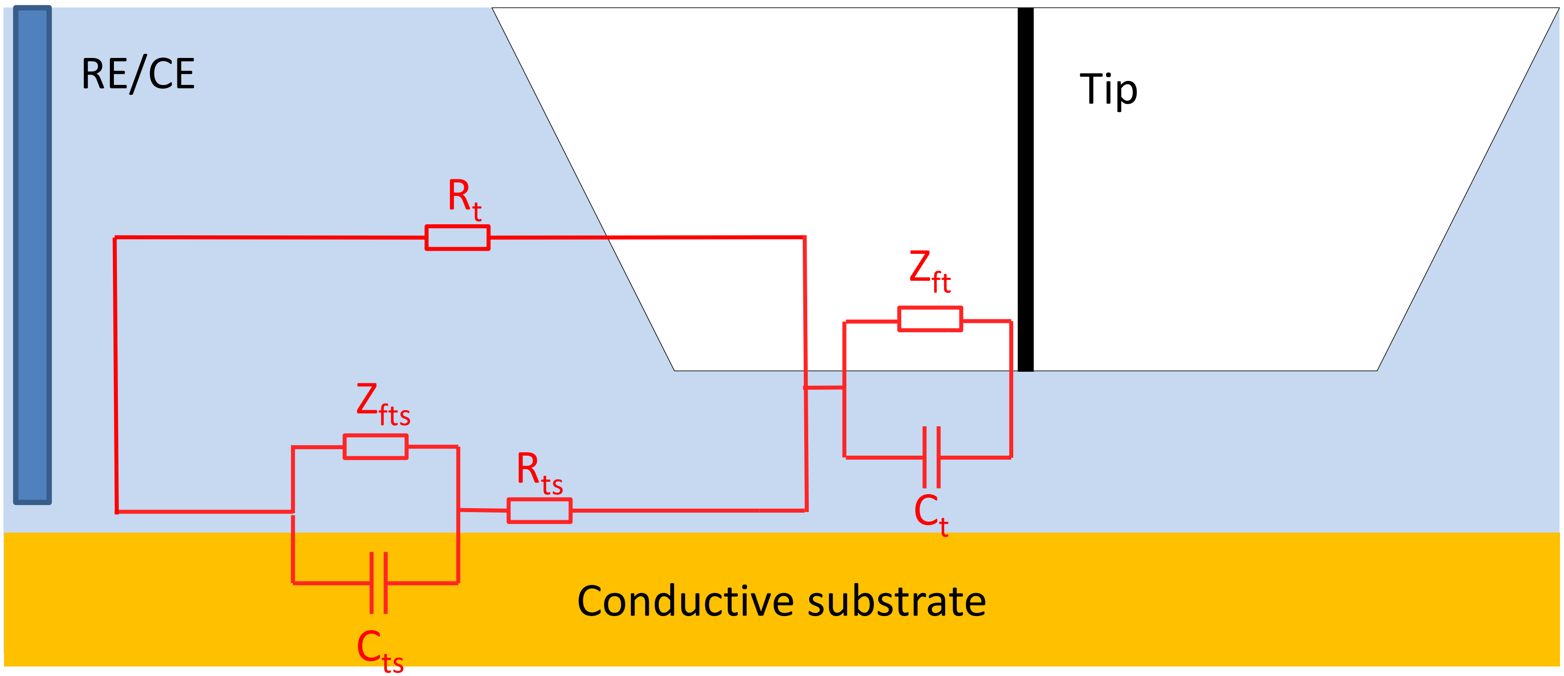
The substrate being much larger than the tip, the impedance of the part of substrate not covered by the tip (Z_{fs}, R_s, C_s) can be neglected.





ac-SECM measurement on a conductive substrate

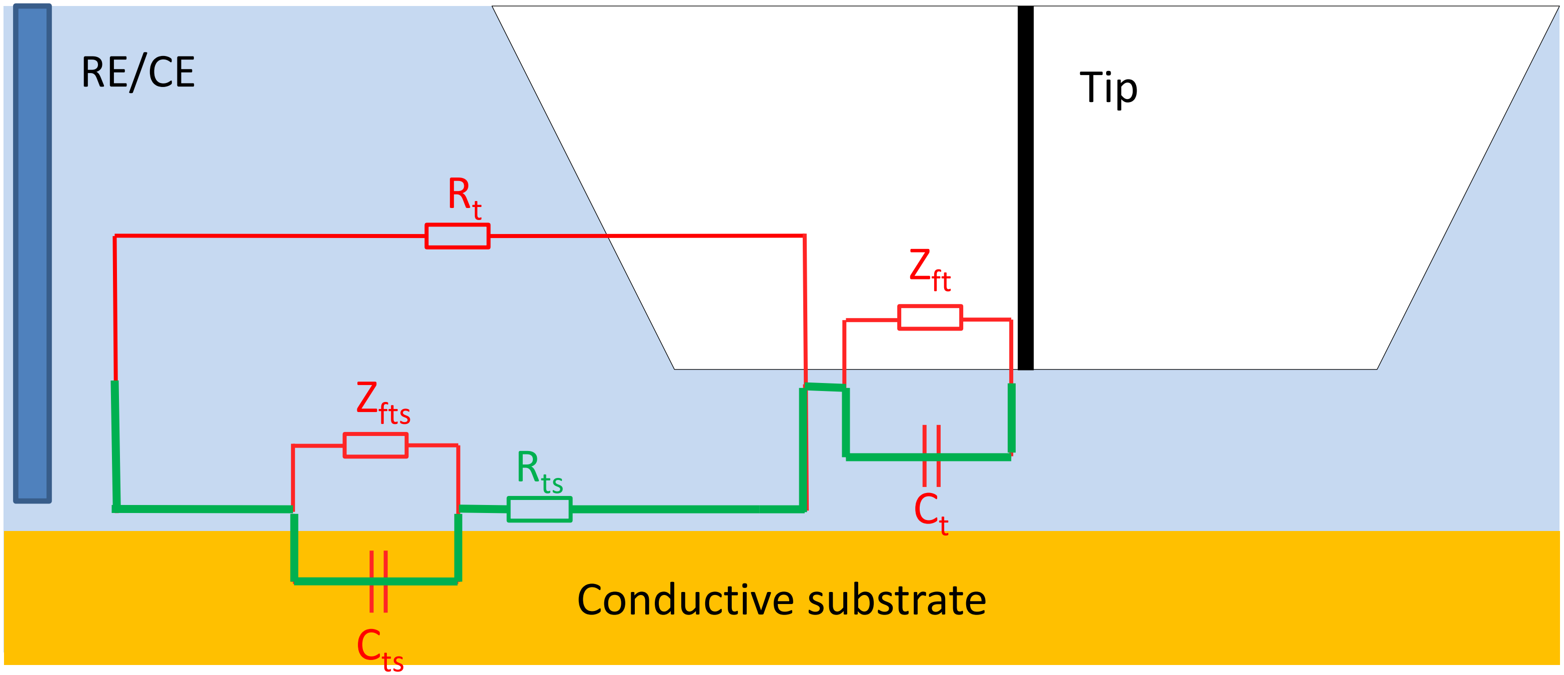
The response of the conductive substrate depends on the conductivity of the electrolyte and the frequency of the perturbation.



ac-SECM measurement on a conductive substrate

At High frequencies and/or low conductivity

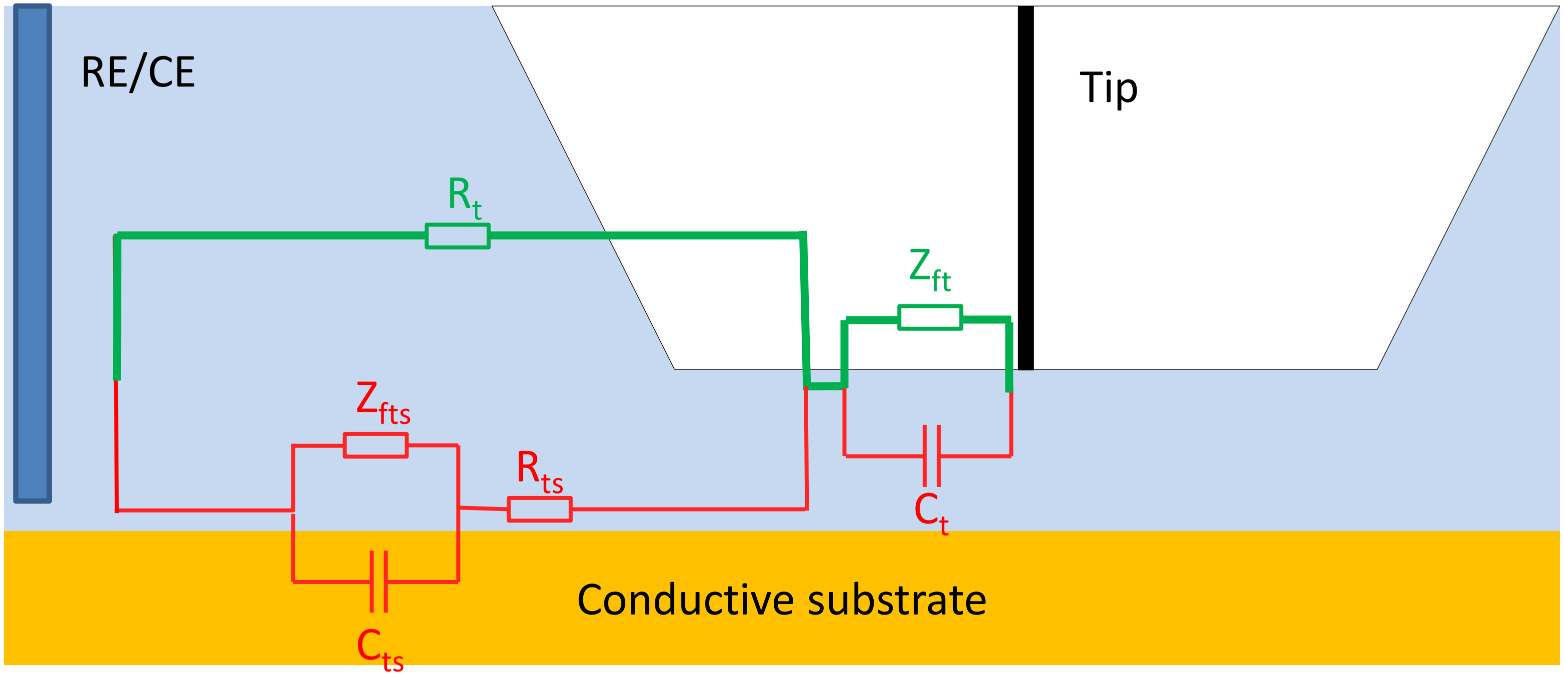
At high frequencies, the capacitances behave as shorts and the current is limited by the value of R_{ts} the solution resistance between the tip and the substrate.
As the tip approaches the surface, R_{ts} decreases and the current response increases.



ac-SECM measurement on a conductive substrate

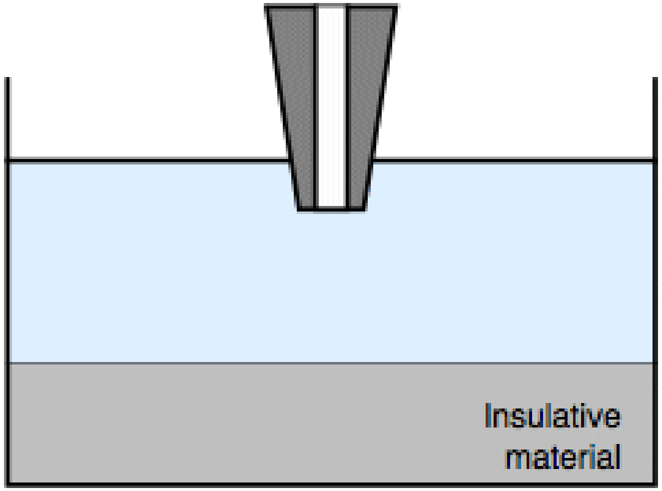
At low frequencies and/or high conductivity

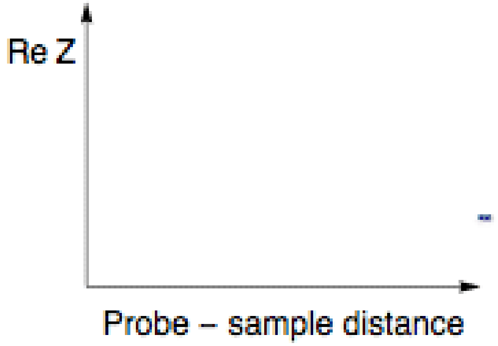
At low frequencies, the current preferably flows, not through the substrate but through the solution and the current is limited by the solution resistance R_t. The conductive substrate behaves as an insulator and the impedance increases and becomes dominant w.r.t. Z_{ft}.



ac-SECM measurement
Summary

Click on figure to see the animation





For all frequencies, Re Z increases when the tip approaches the surface.

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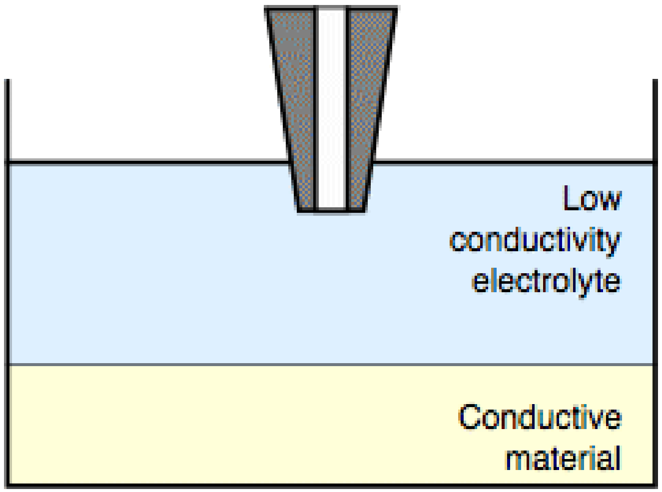

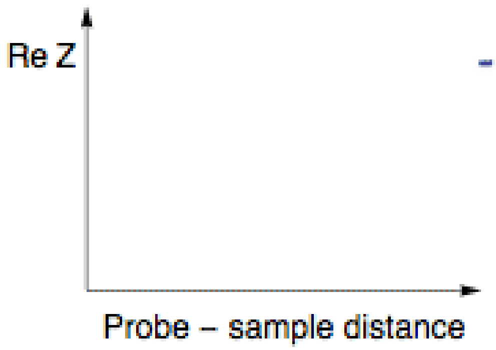

For high frequencies, or low conductivity electrolyte, Re Z decreases when the tip approaches the surface.

ac-SECM measurement
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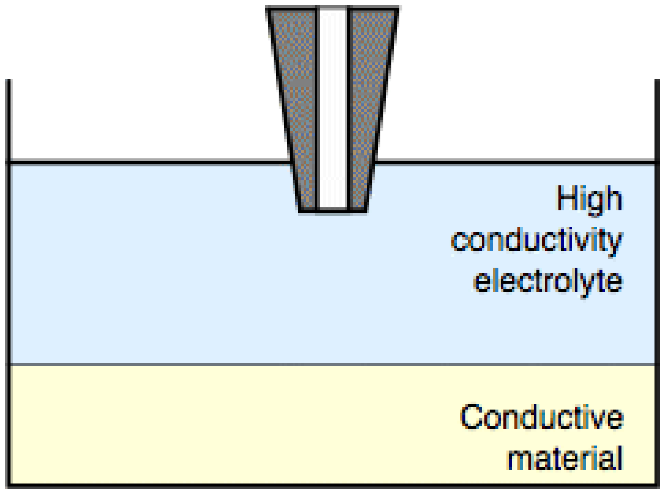

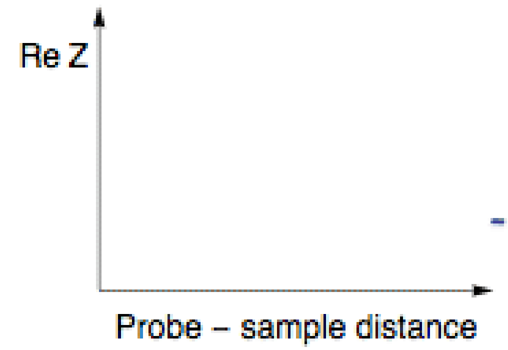

For low frequencies, or high conductivity electrolyte, Re Z increases when the tip approaches the surface.

ac-SECM measurement
Summary

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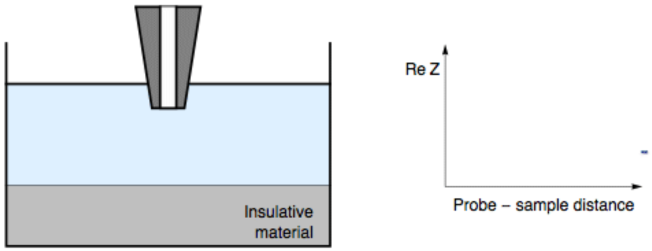
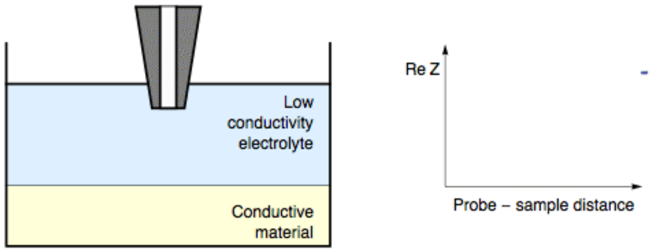
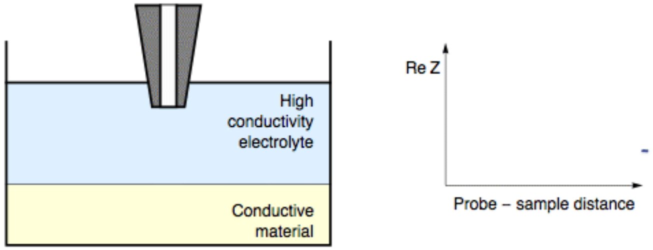


For all frequencies, Re Z increases when the tip approaches the surface.



For high frequencies, or low conductivity electrolyte, Re Z decreases when the tip approaches the surface.



For low frequencies, or high conductivity electrolyte, Re Z increases when the tip approaches the surface.

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ac-SECM measurement

Consequences

1. The impedance can be used to perform topography measurements, for instance by doing constant impedance measurements , or to control the position of the tip.

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2. The local conductivity of a surface can be investigated <u>without mediator</u>.

3. When using a mediator, the impedance can be used to control the tip-to-sample distance while the dc response can be used to image local conductivity. SECM measurements with distance control can be achieved.

Outline

1. Prerequisite : dc-SECM
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1. Determination and control of the position of the probe during SECM measurements

***. B.R. Horrocks et al., Anal. Chem. (1995), 65,* 3605-3614**

They were the first authors to use an ac signal to calibrate the tip-sample distance: 10 kHz in 1 mM KCl.

They performed an approach on a conductive sample, when Re Z decreased by a factor of 2, they considered the tip was touching the substrate.

It allowed positioning of the sample without mediator. They could then map hydrogen peroxide concentrations.

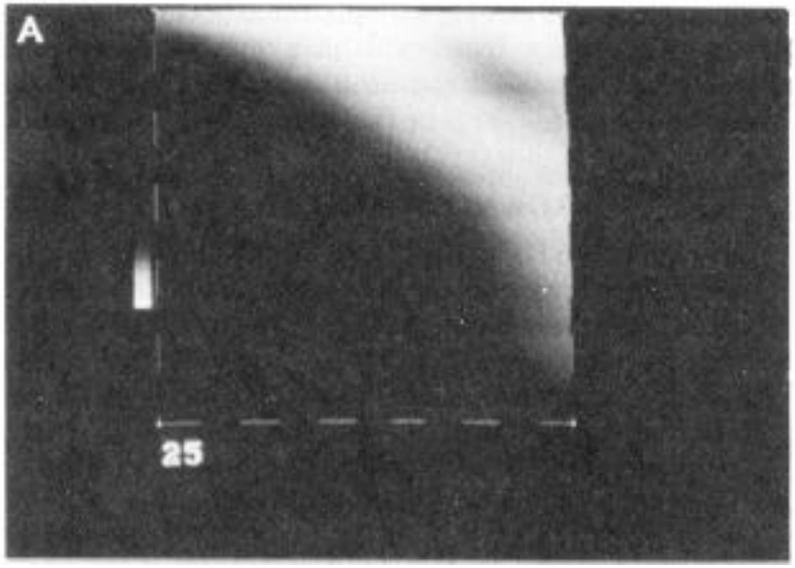
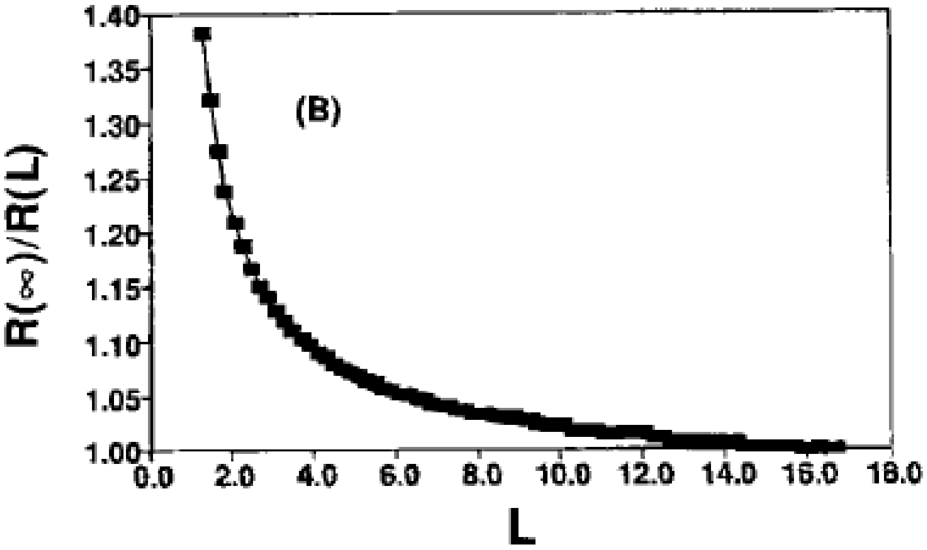


Image of the concentration profile of hydrogen peroxide near the surface of a glassy carbon-platinum composite.

1. Determination and control of the position of the probe during SECM measurements

. C. Wei, A. J. Bard, J. Electrochem. Soc., 142, 8, (1995), 2523-2527

Approach curves were performed in 0.1 M $CuSO_4$ and 10 mM H_2SO_4, using a 2 mV 120 kHz ac perturbation. The value of R can be used (but is not) to monitor thickness change of deposited Cu films.



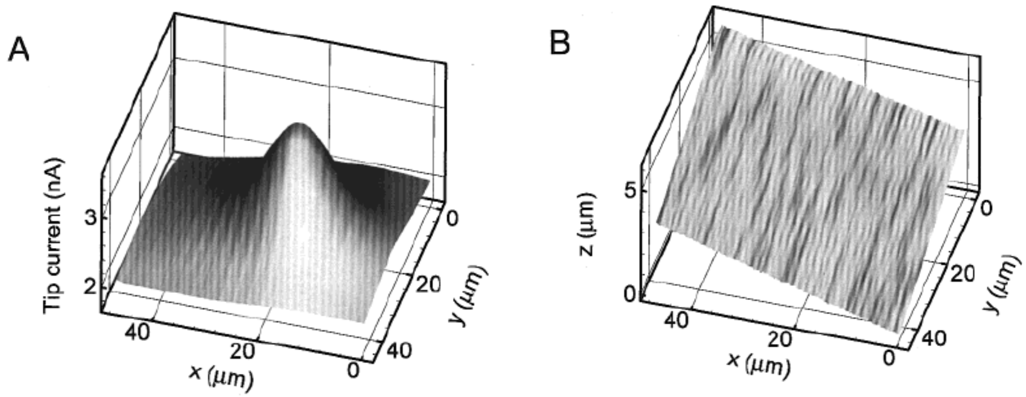
1. Determination and control of the position of the probe during SECM measurements

. M. A. Alpuche-Aviles, D. O. Wipf, Anal. Chem., (2001), 73, 4873-4881

In this case, the ac and dc responses are used simultaneously.

The solution resistance measured by the high-frequency ac response is kept constant and used to measure topography.

The dc current response is measured to obtain the surface conductivity, removing the contribution of the surface height change.



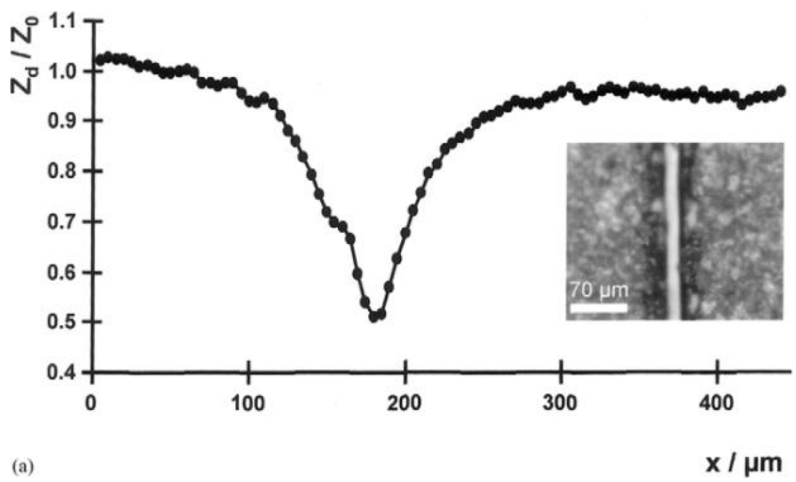
Feedback (A) and topographic (B) height images of a 10 µm diameter Pt disk substrate acquired under impedance feedback control

2. Local electrochemical surface properties

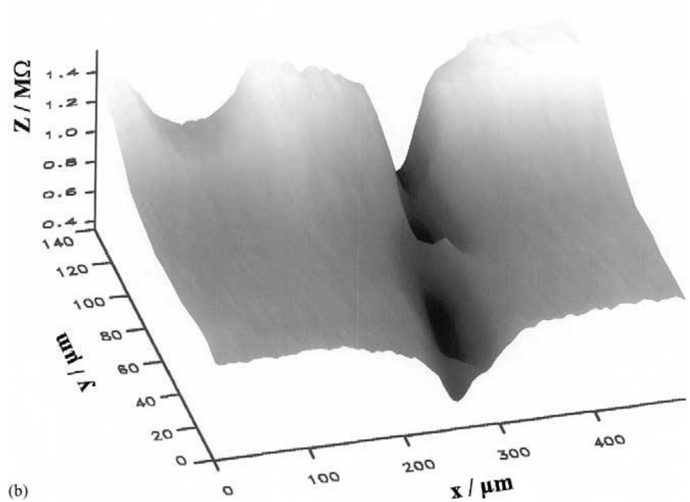
Since ac-SECM is a mediator-free technique, it can be used to investigate freely corroding surfaces.
It was coined 4D-SECM by Schuhmann, the 4th dimension being the frequency.
It is used in constant-height mode to detect a scratch in the lacquer.

Katemann et al., Electrochim. Acta 48 (2003) 1115-1121

A)



B)



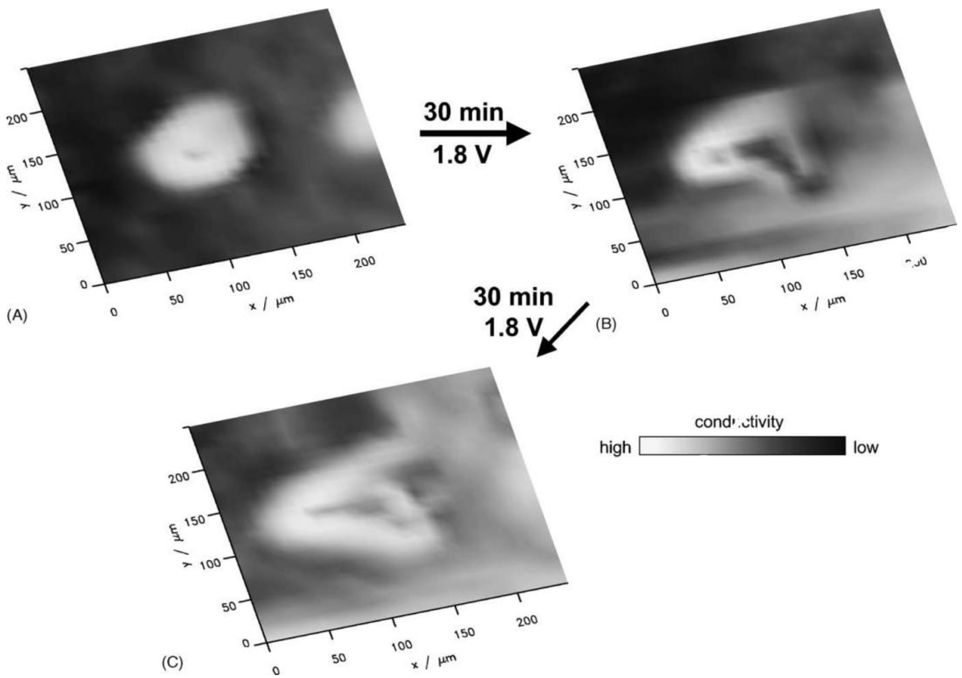
Lacquered tin plates

A) A single line-scan displaying the modulus Z) as a function of the tip position in x-direction. Inset: optical image of the scratch.
B) 3D-image of the scratch shown in (A) obtained with ac-SECM in a constant-height mode.

2. Local electrochemical surface properties

Another paper by Schuhmann shows the study of the corrosion of oxide-covered Ni-Ti memory shape alloys. Inhomogeneities are imaged using ac-SECM at 1 kHz.

A. Schulte et al., Mat. Sci. and Eng. A 378 (2004) 523–526



The brighter regions correspond to areas of decreased solution resistance R_{sol}, thus a higher local surface conductivity.

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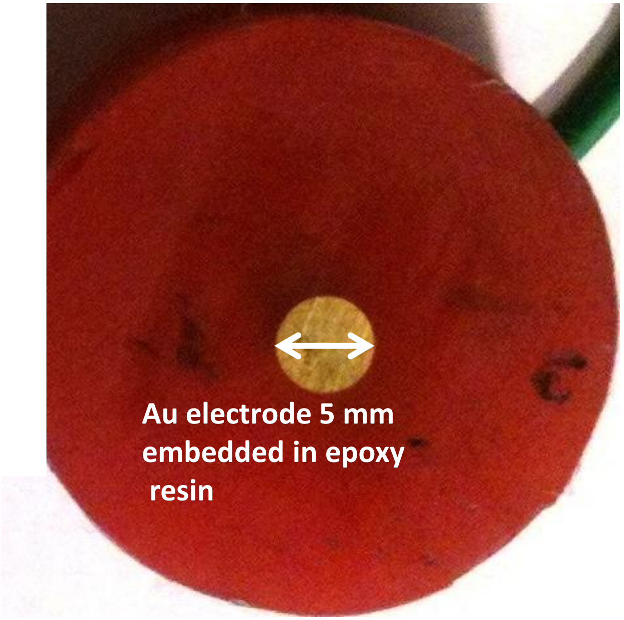
ac-SECM : M470 maps

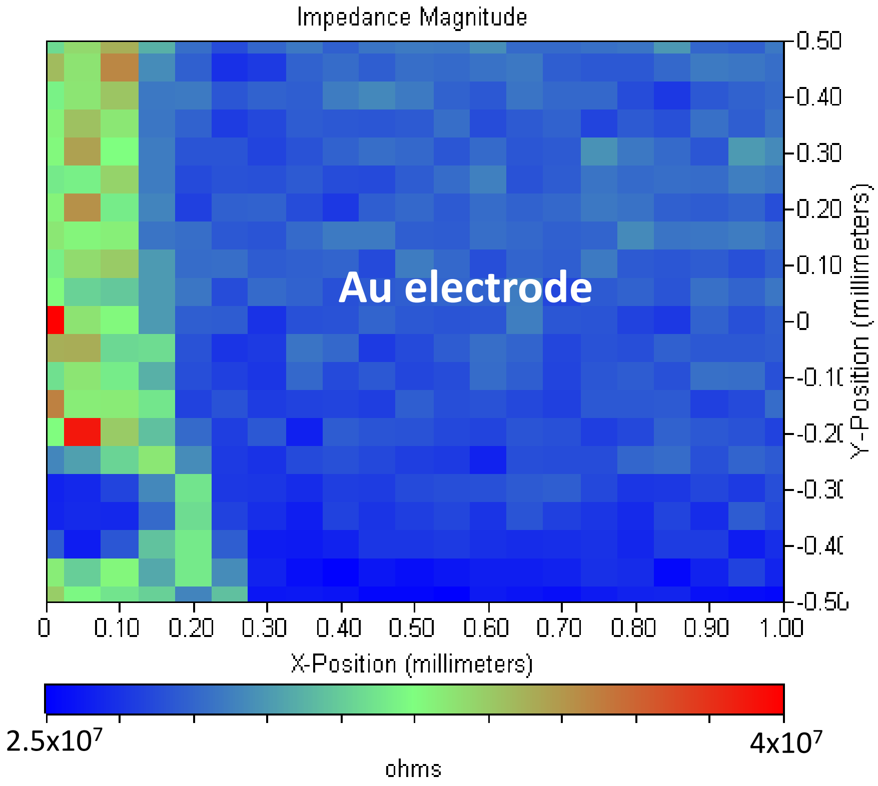
Sample :

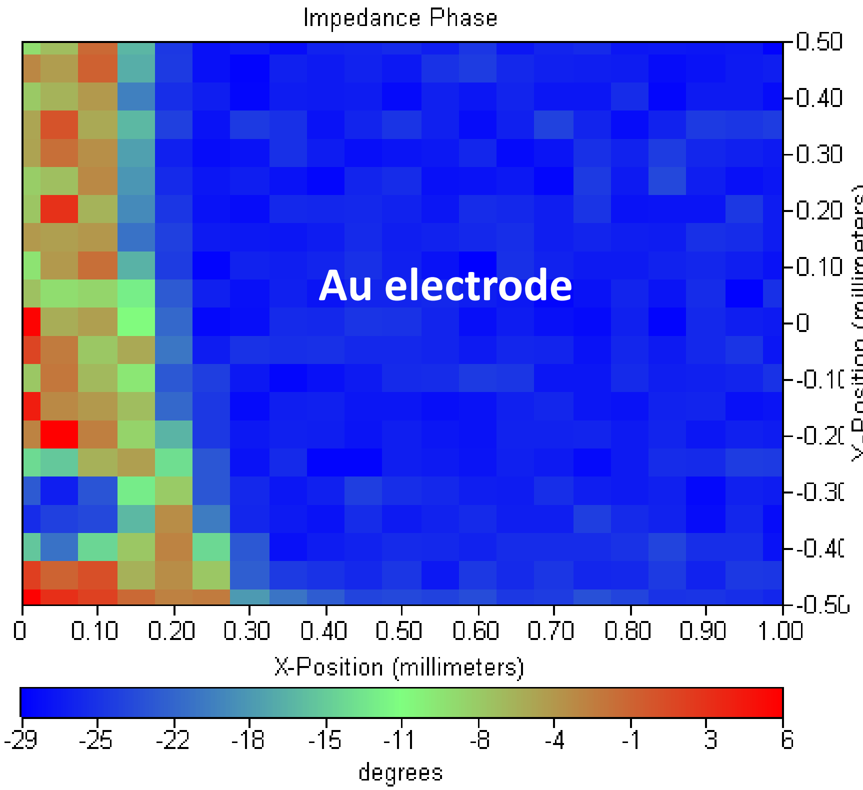


10 mM Fe^{III}/Fe^{II}, 100 mM KCl
25 µm UME
Probe polarized at 50 mV *vs.* OCP
ac modulation : 100 mV amplitude @ 5 kHz
Sample at OCP

ac-SECM : M470 maps

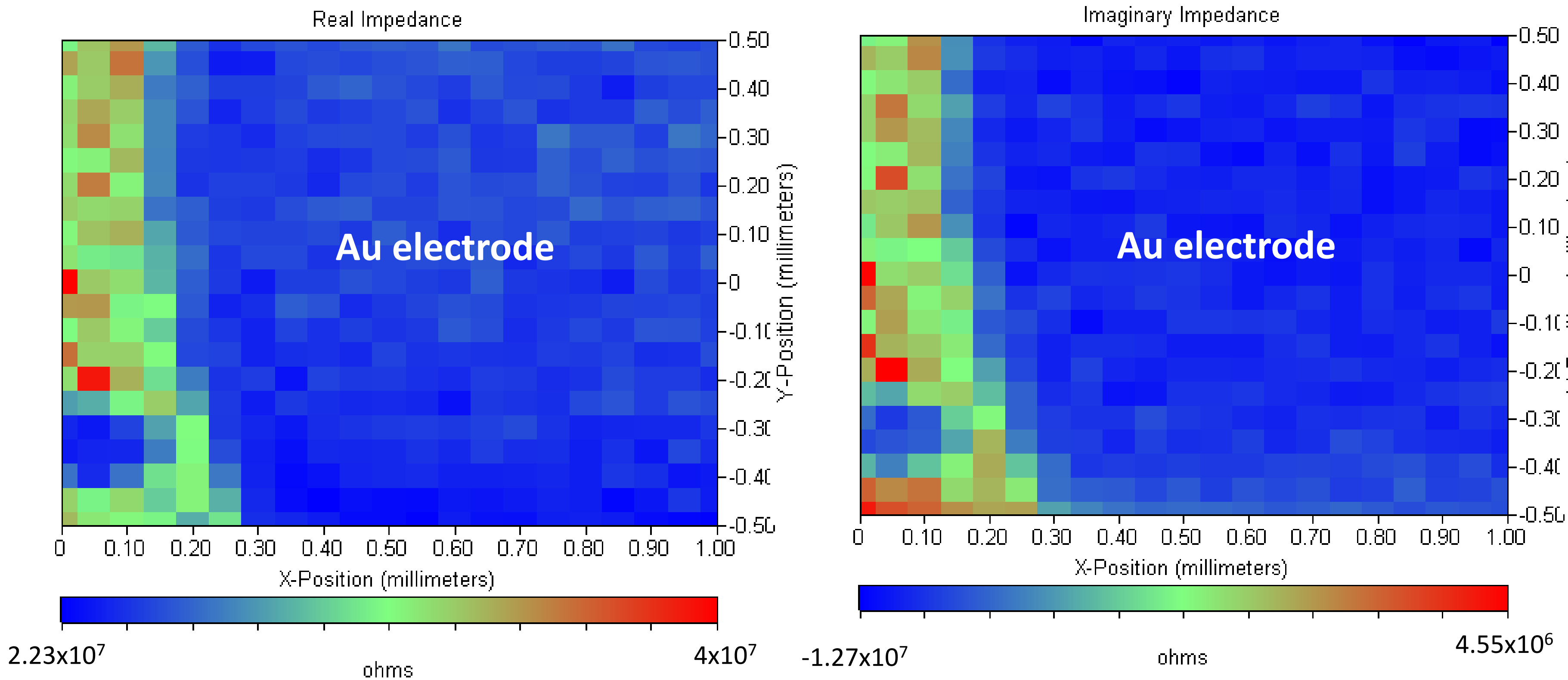
The procedure is the same as SECM.
The approach curve obtained by measurement of |Z| will soon be available.
ac-SECM area map show the value of |Z| and the phase at one frequency over the sample.





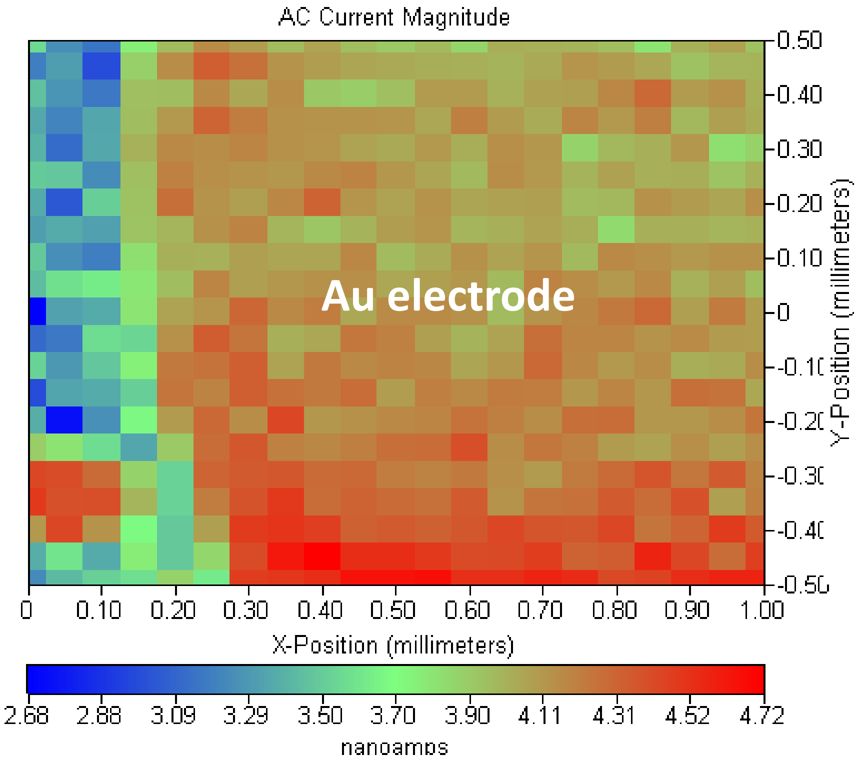
ac-SECM : M470 maps

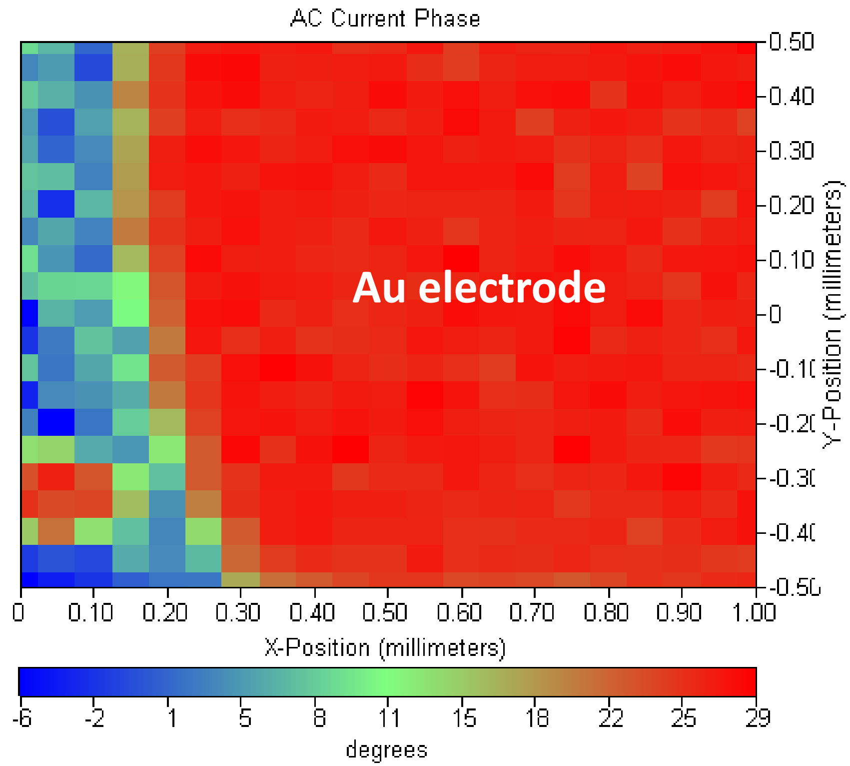
ac-SECM area map can also show the value of Re Z and Im Z.



ac-SECM : M470 maps

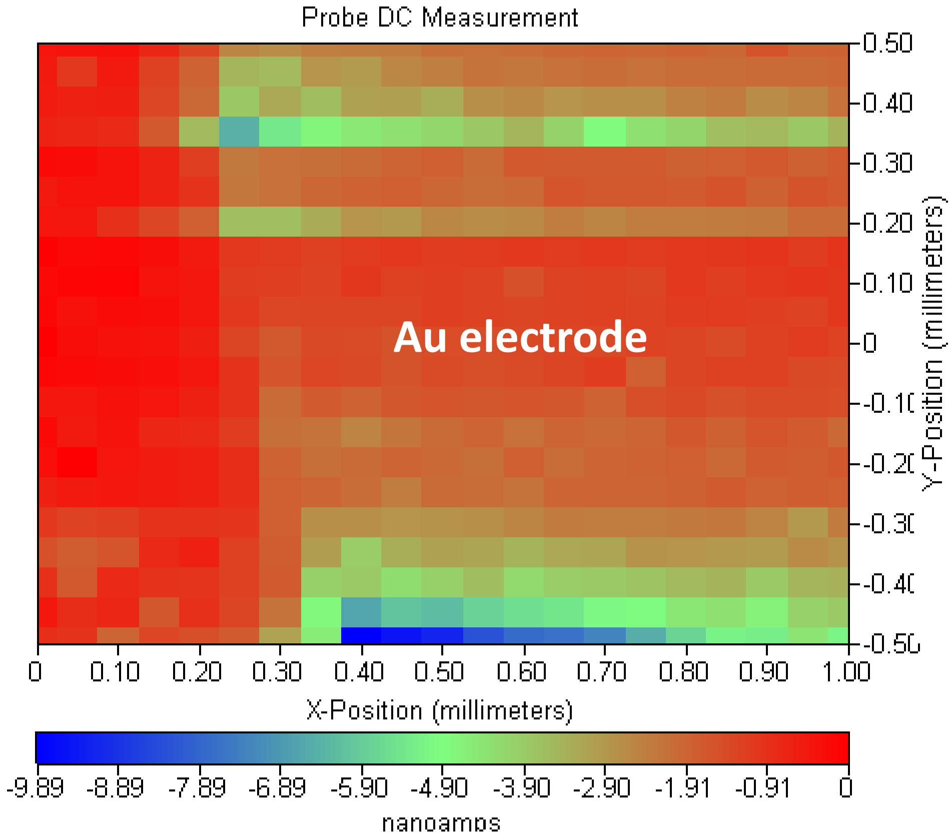
ac-SECM area map can also show the value of |Iac| and the current phase at one frequency over the sample.





ac-SECM : M470 maps

The contrast in the dc response is not as good due to the small overpotential applied to the probe.



Conclusions

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- The UME response depends on the conductivity of the sample, the frequency of the modulation, the conductivity of the solution.
- ac-SECM does not require the use of a mediator.
- It can be used to estimate the probe to sample distance during a dc-SECM measurement.
- It can be coupled to ic-SECM for an increased contrast.