# How to get clear images in Scanning Electrochemical Microscopy (SECM)*

## Part 2: Experimental Considerations

Version 1.0

*dc-SECM advice made within this tutorial can be applied to dc-SECM measurements on the M470, SECM150, and M370 instruments

# Aim.

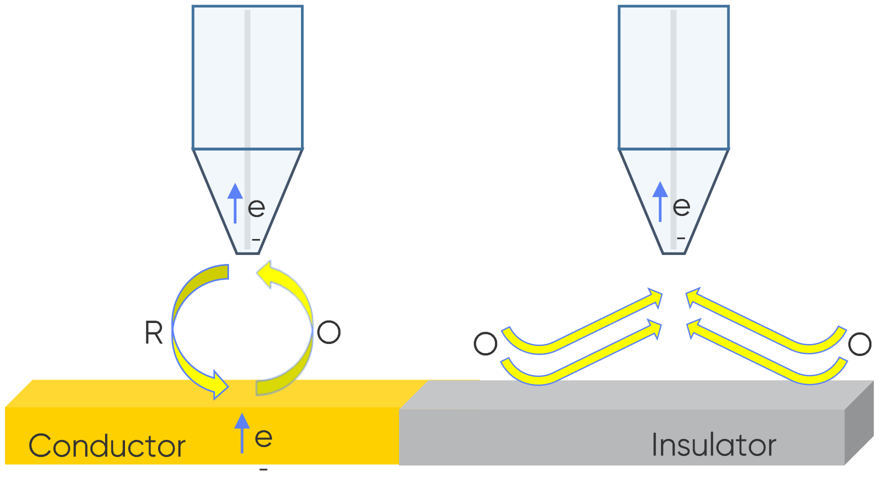
This two part tutorial aims to provide users with the information they need to obtain clear images using Scanning Electrochemical Microscopy (SECM). In this part we address a number of experimental factors which can affect the SECM image. Generally these include the type of SECM experiment performed, and the experiment conditions. Each factor must be optimised to obtain a clear SECM image. Once mastered users will be able to measure model and novel samples.

# Order of optimization.

- **Determine if dc-SECM or ac-SECM will be used.**
- **If dc-SECM:**
  - Decide if mediator should be added to electrolyte
  - Decide which mediator to use
  - Determine probe bias
  - Determine if sample needs to be biased
- **If ac-SECM:**
  - Select electrolyte
  - Choose measurement frequency
- **Determine if the experiment will be run in constant height or constant distance mode.**

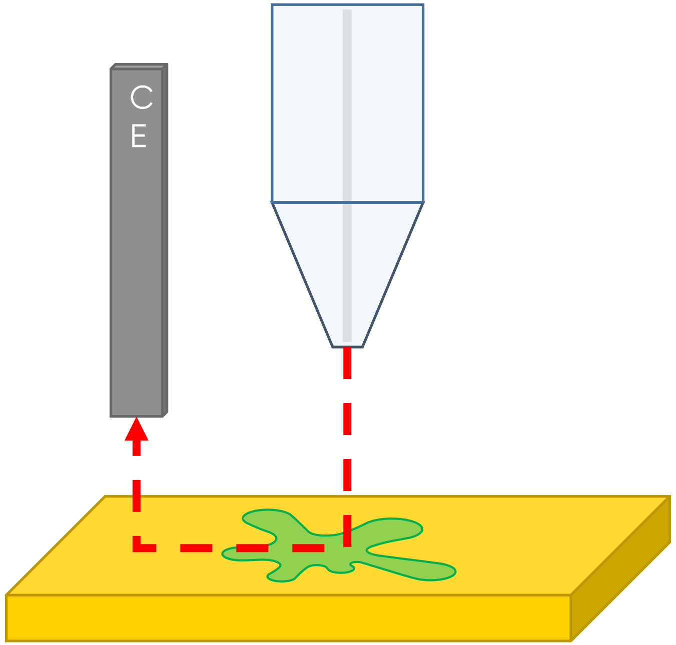
# dc-SECM or ac-SECM?

# Direct Current – Scanning Electrochemical Microscopy: dc-SECM.




**dc-SECM uses an UltraMicroElectrode (UME) probe in close proximity to a sample surface to measure the electrochemical activity of a sample. The probe is biased to interact with a redox mediator, allowing for the measurements to be chemically selective.**

# Alternating Current – Scanning Electrochemical Microscopy: ac-SECM.




In ac-SECM a sinusoidal bias is applied to an UltraMicroElectrode (UME) probe held in close proximity to a sample surface. The probe impedance is measured, which depends on the surface conductivity.

ac-SECM does not require the use of a redox mediator.

# dc-SECM or ac-SECM?

## When to use dc-SECM:

- Interested in the activity of a sample with regards to a specific redox reaction
- Sample produces electroactive species (e.g. in corrosion)
- For the fastest possible measurement

## When to use ac-SECM:

- Interested in sample conductivity in a specific environment
- Sample interacts poorly with typical redox mediators
- Difficulty finding a usable redox mediator
- Want to measure in low conductivity solutions (e.g. tap water)

# Considerations for dc-SECM.

# Selecting the redox mediator.

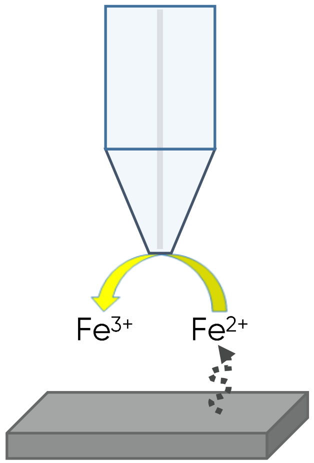
# How is a mediator selected?

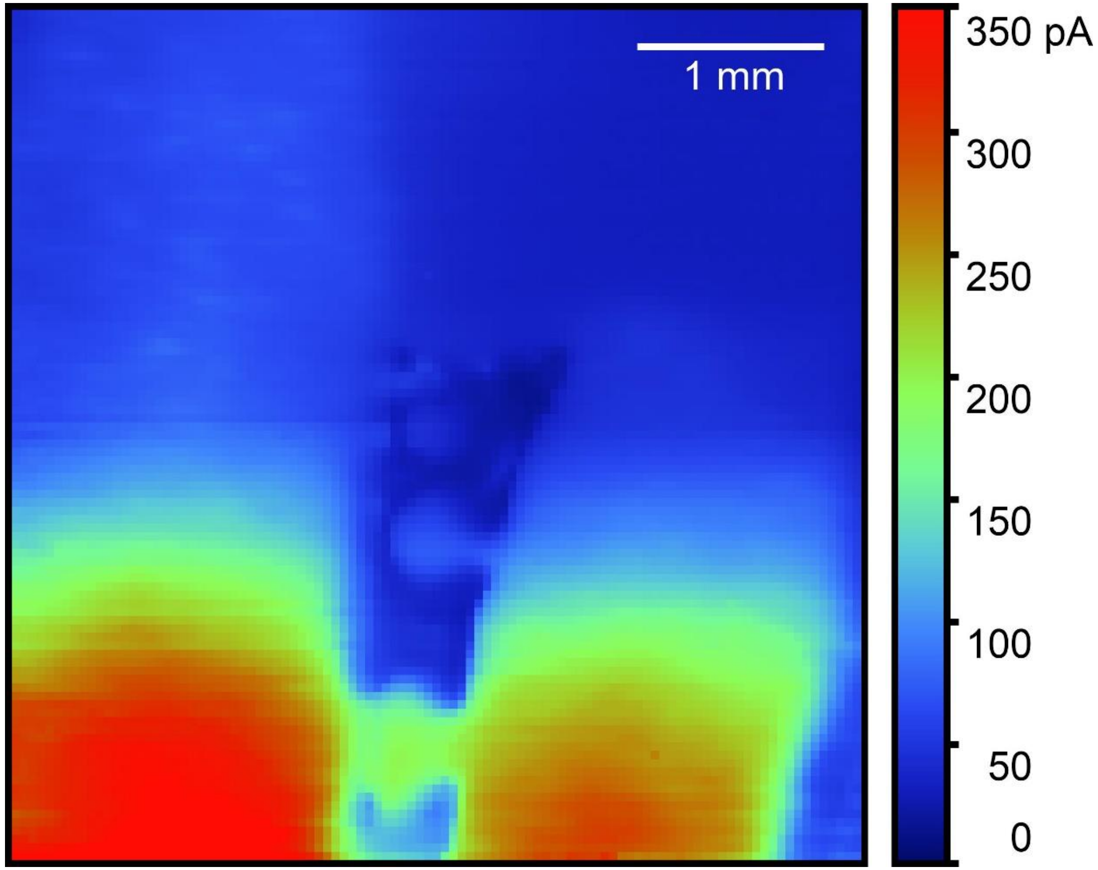
When selecting a redox mediator a number of questions need to be answered:

- Does a mediator need to be added to the electrolyte?
- Is a particular electrochemical redox interaction of interest?
- Is there a poor interaction between the mediator and the sample?
- Is the mediator stable under the selected experimental conditions?
- Is the redox reaction of the mediator diffusion controlled?

# Does a mediator need to be added to the electrolyte?

**A mediator is not required if an electroactive species is produced by the sample. For example $Fe^{2+}$ produced during corrosion of steel.**

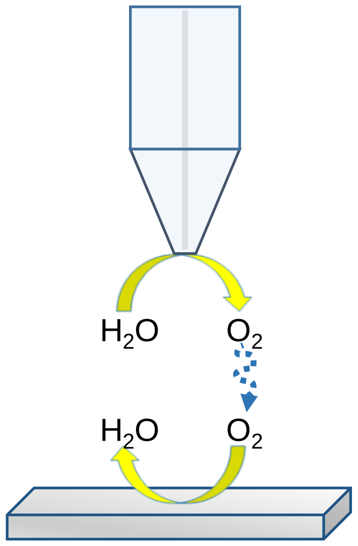


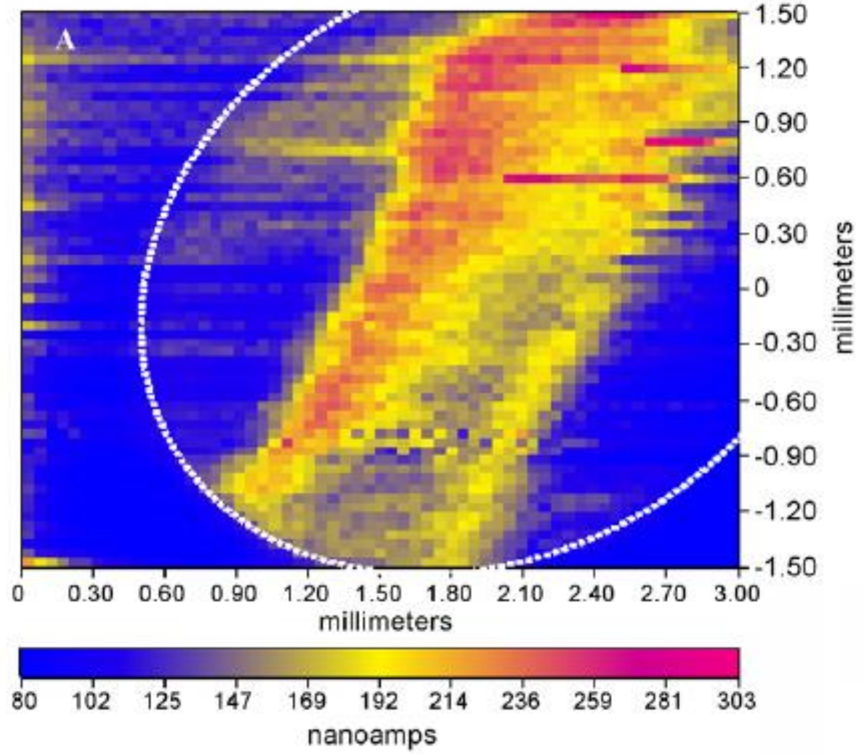




*Steel weld sample in 0.1 M NaOH. The probe is biased at 0.6 V vs Ag/AgCl to oxidize $Fe^{2+}$ to $Fe^{3+}$.*

# Is a particular electrochemical interaction of interest?

**The electrochemical selectivity of dc-SECM means it can investigate specific interactions between a sample and a redox mediator. This is the case for catalysis studies in which the sample is catalytic towards the redox mediator.**



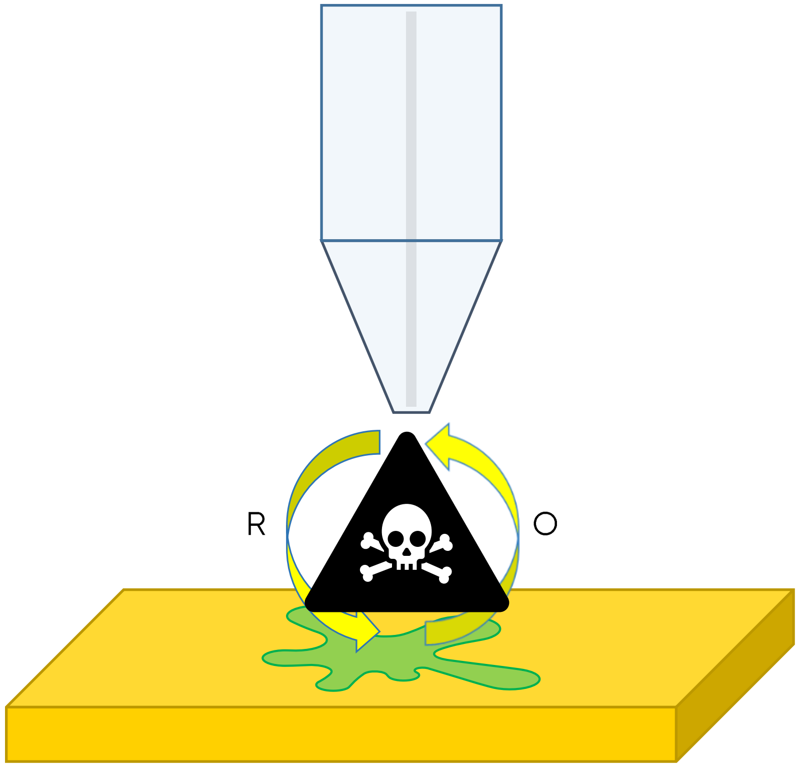




*Enhanced oxygen reduction over catalytic Pt stripe in 0.5 M $H_2SO_4$.*

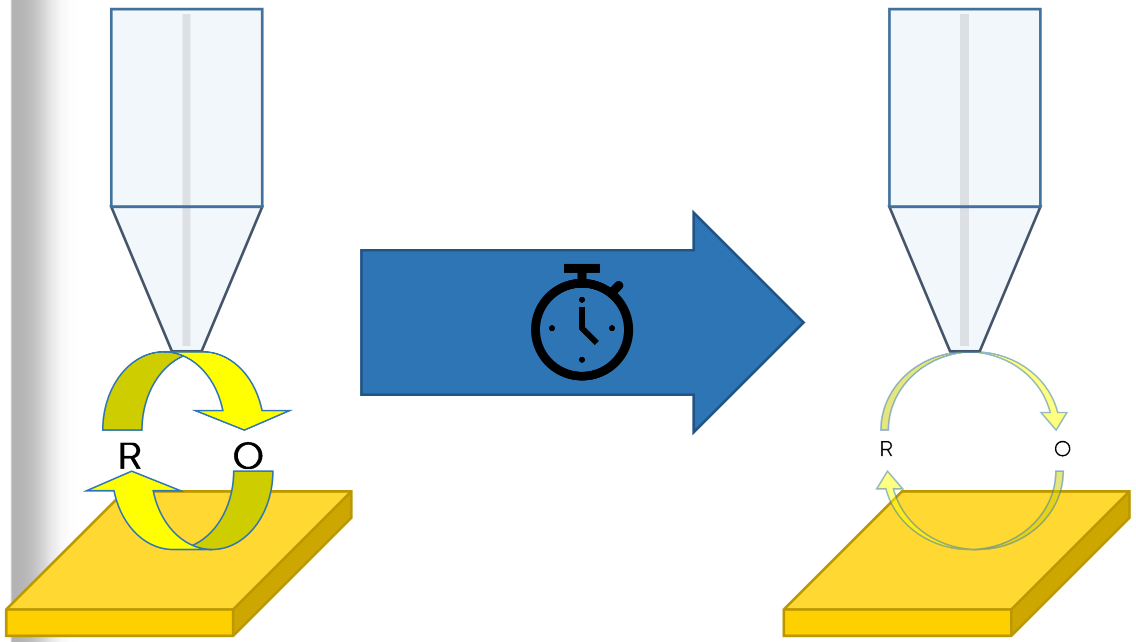
From: G. Lu, J. S. Cooper, P. J. McGinn, *Electrochim. Acta* 52 (2007) 5172–5181

# Is there a poor interaction between the mediator and the sample?

Some mediators can be ruled out because they interact poorly with the sample of interest. For example the effect of added redox mediators on the rate of the corrosion cannot be necessarily ruled out. Furthermore, many mediators, such as $[Ru(NH_3)_6]Cl_3$, are often toxic to living cells.

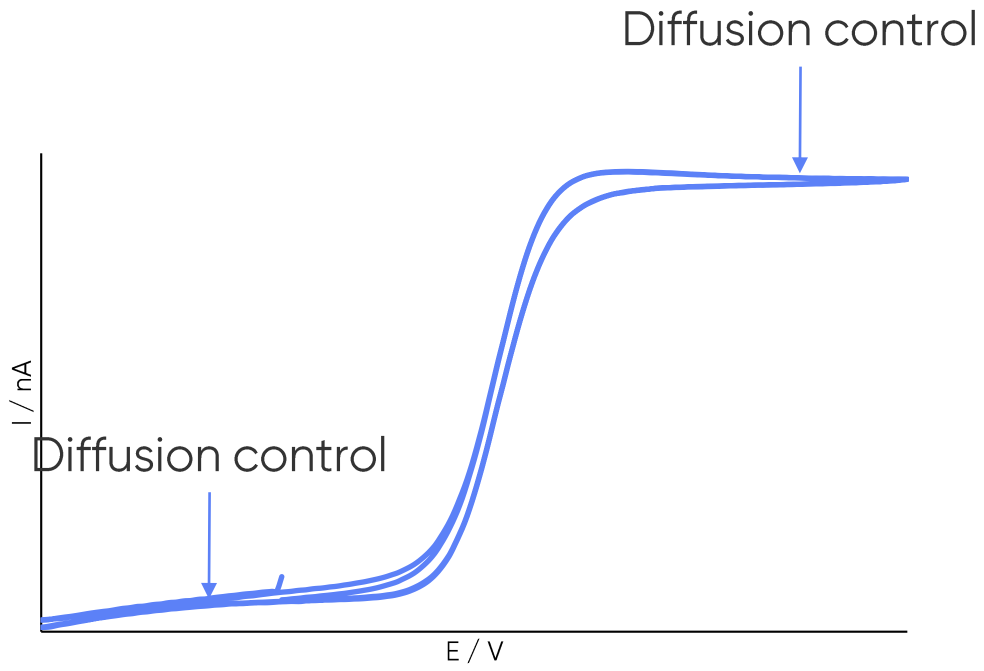


# Is the mediator stable under the selected experimental conditions?




The mediator must be selected to be stable in the experimental conditions including electrolyte medium, atmospheric conditions, and bias potential. If the mediator decays during the experiment the signal will be poor. For example when used on its own the current measured using the Ferrocyanide mediator can sharply decline during an experiment. This is resolved with the addition of an equal concentration of Ferricyanide.

# Is the redox reaction under diffusion control?




**The clearest SECM images require the redox reaction of the mediator to be under diffusion control in the electrochemical window of interest.**

# Some example redox mediators.

## The redox mediator can be any electrochemically active molecule, some examples are given.

| Mediator | Redox reaction | $E^0$ (V vs. Ag/AgCl) |
|---|---|---|
| FcMeOH (Ferrocene Methanol) | $[FcMeOH]^+ + e^- \rightarrow FcMeOH$ | 0.303 |
| $Fe(CN)_6$ (Ferricyanide) | $[Fe(CN)_6]^{4+} + e^- \rightarrow [Fe(CN)_6]^{3+}$ | 0.294 |
| I (Iodide) | $I_3^- + 2e^- \rightarrow 3I^-$<br>$I_2 + 2e^- \rightarrow 2I^-$ | 0.766<br>0.335 |
| $O_2$ (Oxygen) | $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$<br>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | -0.584<br>-0.440 |
| $Ru(NH_3)_6$ (Runthenium Hexamine) | $[Ru(NH_3)_6]^{3+} + e^- \rightarrow [Ru(NH_3)_6]^{2+}$ | -0.256 |

**For a thorough list of redox mediators used in SECM please see D. Polcari, P Dauphin-Ducharme, J. Mauzeroll, *Chem. Rev.* 116 (2016) 13234–13278**

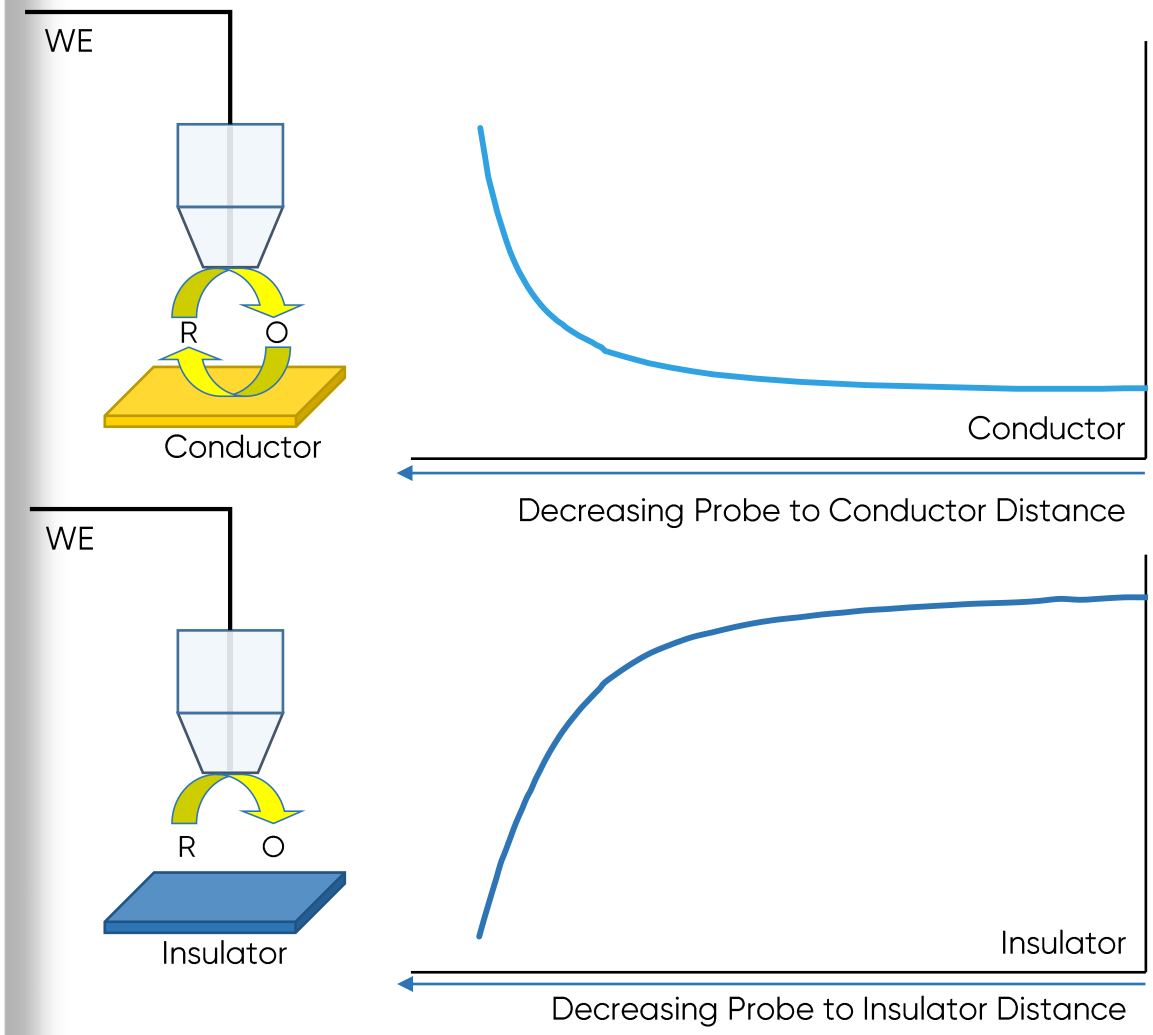
# Selecting dc-SECM mode.

# dc-SECM modes.

dc-SECM can be performed in a number of different modes which will be discussed:

- Feedback mode
- Substrate Generator/Tip Collector mode
- Tip Generator/Substrate Collector mode
- Competition mode
- Direct mode

# Feedback (FB) mode – Background.




- Most common mode
- Diffusion controlled measurement of redox mediator added to solution
- Probe biased to interact with mediator
- Sample remains unbiased
- Positive feedback over conductor and negative feedback over insulator

# Feedback (FB) mode – Pros & Cons.

## Pros:

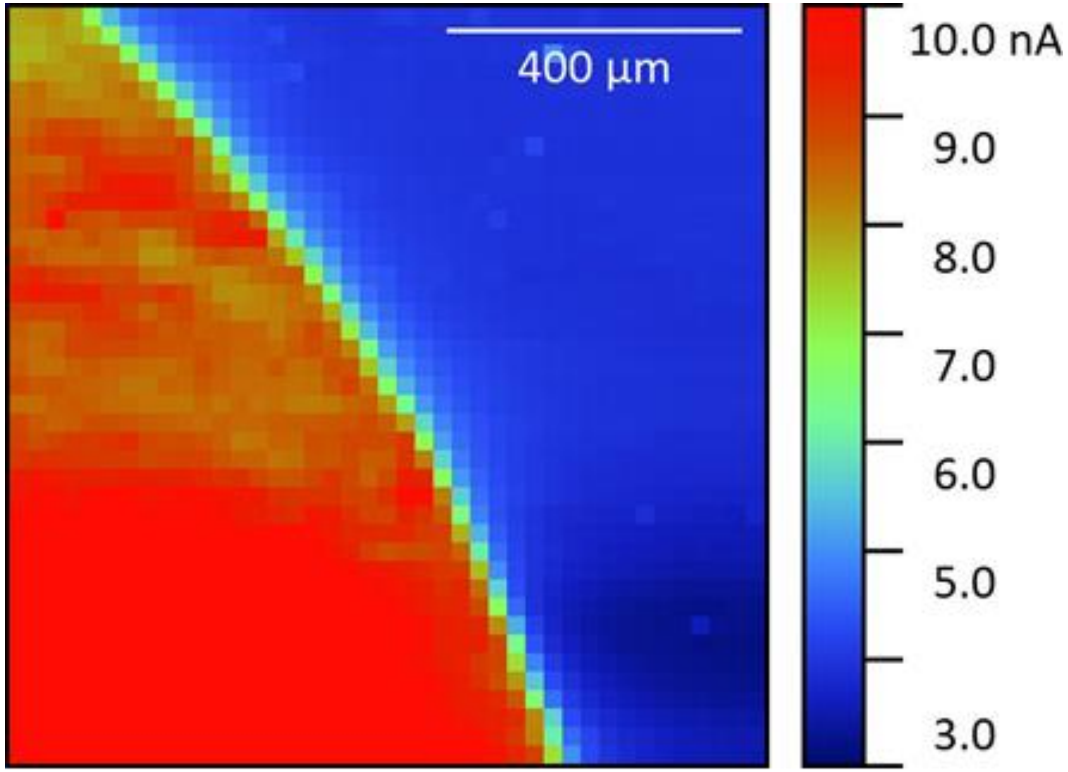
- Simplest SECM setup
- No activity requirement for sample
- No need to connect to sample

## Cons:

- Highly dependent on probe to sample distance
- Signal is a mix of activity and topography when used in constant height mode

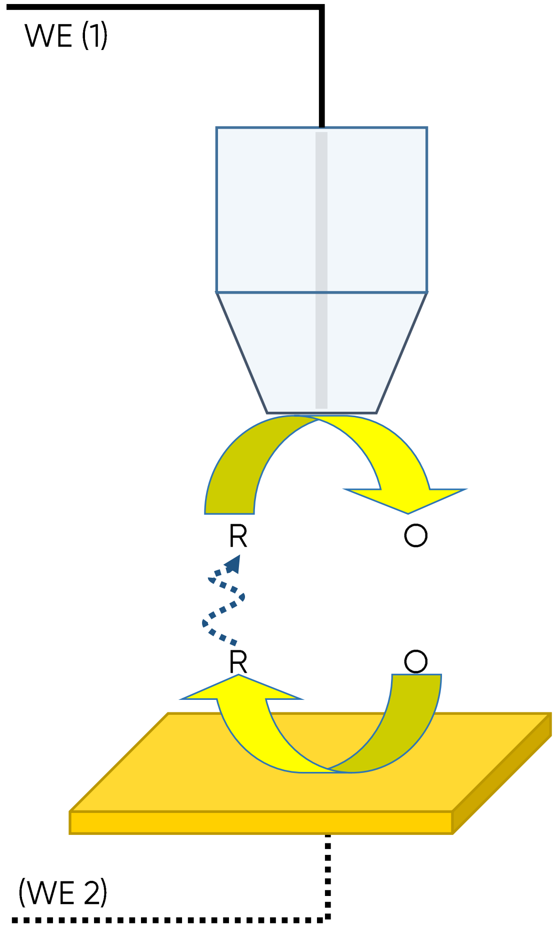
# Feedback (FB) mode – Uses.

- Has been used in most application areas
- Good for relatively flat samples
- Useful for measuring samples with conducting regions isolated in large insulating regions.




*Au in resin sample in 2.5 mM $K_3[Fe(CN)_6]$ and 2.5 mM $K_4[Fe(CN)_6]$ in 100 mM KCl. The probe is biased at 0.65 V vs SCE.*

# Substrate Generator/Tip Collector (SG/TC) mode – Background.



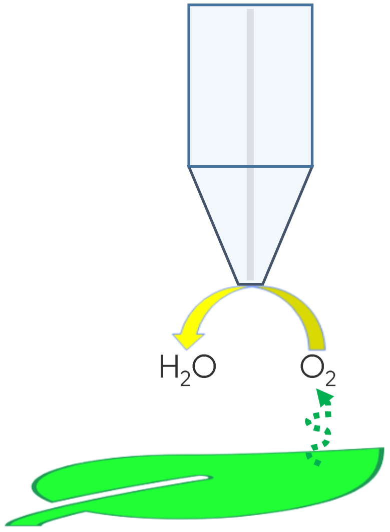

- Substrate *generates* the species which the tip is biased to *collect*
- This species is not originally contained in the solution
- Measurement occurs when the probe moves through the diffusion layer of the substrate
- Commonly performed using both the probe and sample as the working electrode

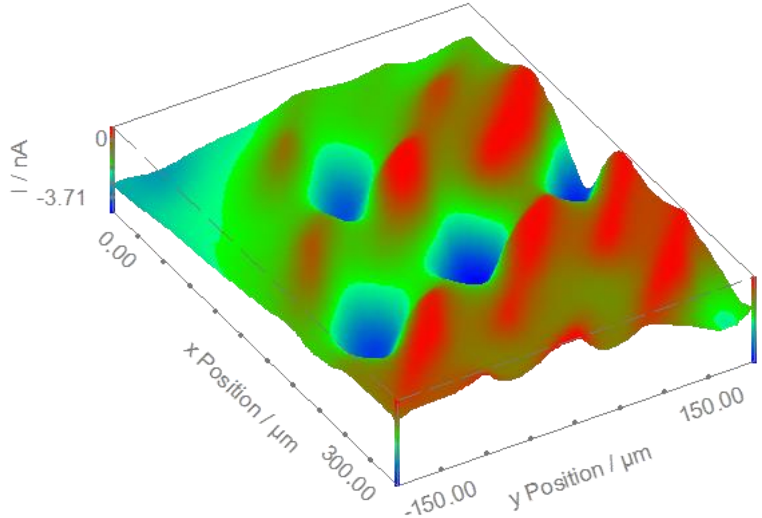
# Substrate Generator/Tip Collector (SG/TC) mode– When to add precursor species to solution

- The precursor species added to solution interacts with the sample to produce a redox active species which interacts with the probe
- The precursor species does not necessarily need to be electrochemically active, however it must interact with the sample to produce an electrochemically active species
- The sample may be biased to convert a redox active precursor
- Some examples where precursor species are added to solution:
  - Investigation of catalytic systems
  - Investigation of the activity of microelectrode arrays
  - Investigation of passive layers

# Substrate Generator/Tip Collector (SG/TC) mode – Uses.

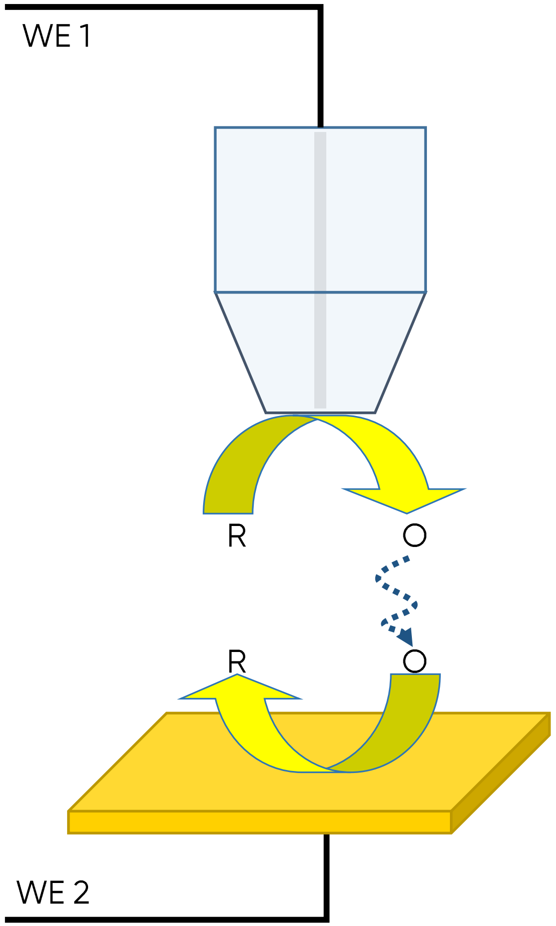
- **Useful for the measurement of concentration profiles, and flux of electrochemical species during a reaction**
- **Applied to**
  - Corrosion
  - Enzymes
  - Catalysis




*Underside of spider plant leaf in 100 mM KCl. The probe is biased at -0.75 V vs SCE to interact with $O_2$.*

# Tip Generator/Substrate Collector (TG/SC) mode – Background.

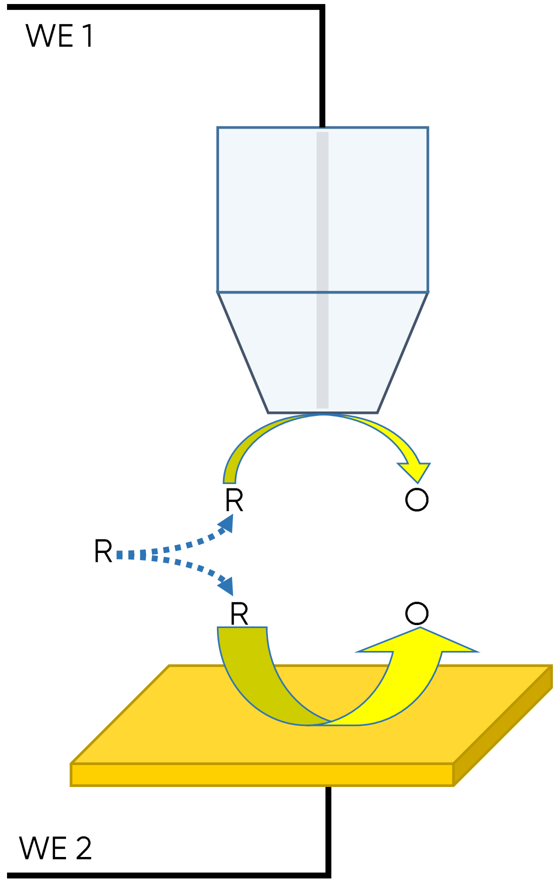



- Tip *generates* the species which the substrate is biased to *collect*
- The species is not regenerated at the tip
- Typically both the probe and sample are WE
- Tip can be a pipette filled with species of interest

# Tip Generator/Substrate Collector (TG/SC) mode – Uses.

- **Less common than Substrate Generator/Tip Collector**
- **Typically used for:**
  - Studies of reaction kinetics
  - Catalysis studies
  - Surface modification

# Competition mode – Background.

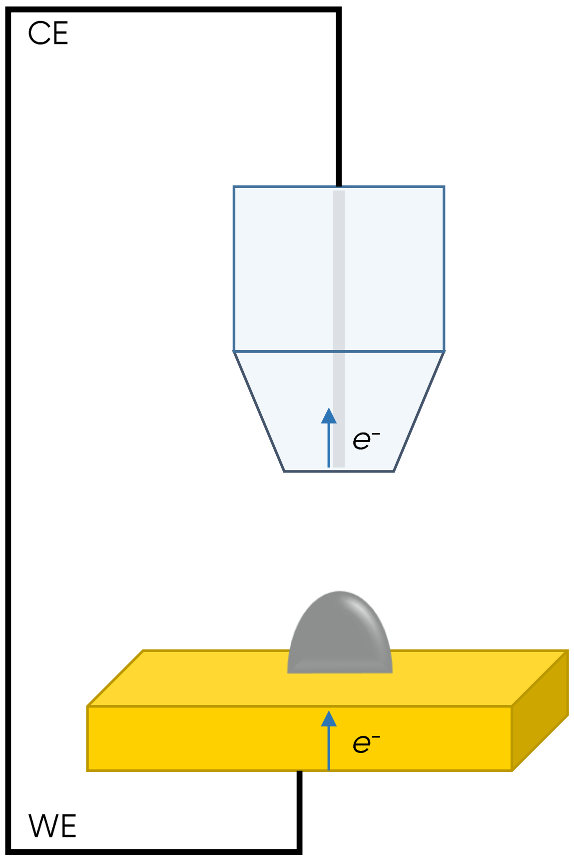



- Also known as Redox Competition mode SECM (RC-SECM)
- Probe and substrate both interact with the same redox mediator
- Redox mediator is already in solution
- Typically both the probe and substrate are WE
- A decrease in current measured at the probe indicates increased substrate activity

# Competition mode – Uses.

- **Competition mode is used to measure the local ability of a substrate to interact with a redox mediator**
- **It has found use in catalysis and corrosion studies**
  - For example in corrosion studies the measurement of oxygen reduction by the probe is of interest. The probe will measure a high current until it moves over an active region on the surface which consumes oxygen, causing a drop in the measured current.
- **Limited by the significant background current of the substrate**

# Direct mode.



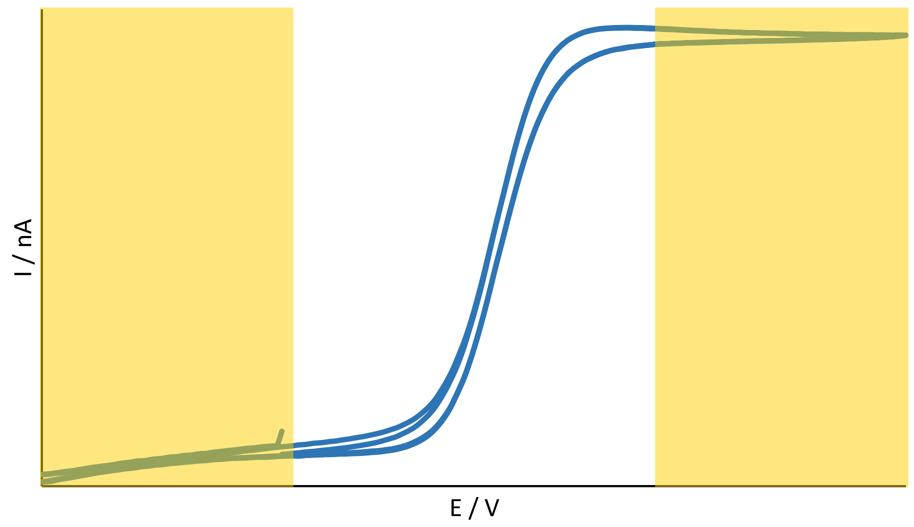

- Three electrode cell with substrate connected as WE and probe as CE
- Localises electric field between probe and sample
- Used for substrate modification including etching, deposition, and patterning.

# Other factors.

# Selecting a measurement potential.

## Selected potential should be:

- In diffusion controlled region
- Away from any other reactions
- Within the electrochemical window

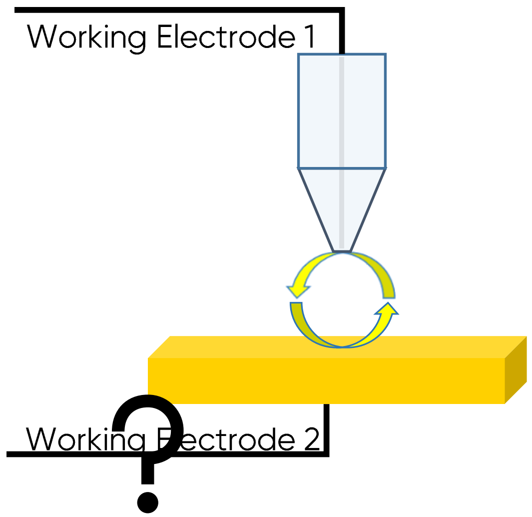



Options for measurement potential

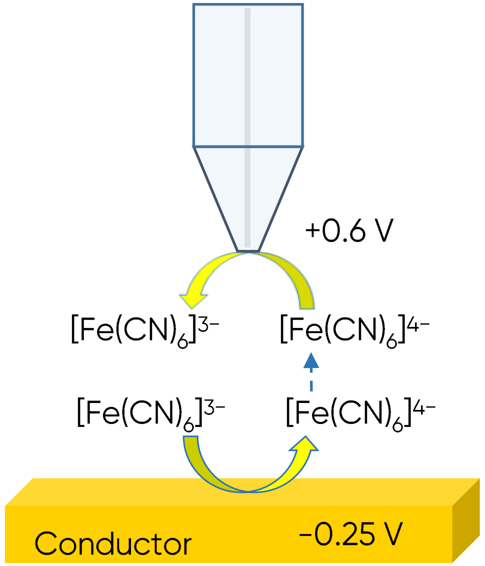
# Should the sample be biased?

In SECM it can help to bias the sample:

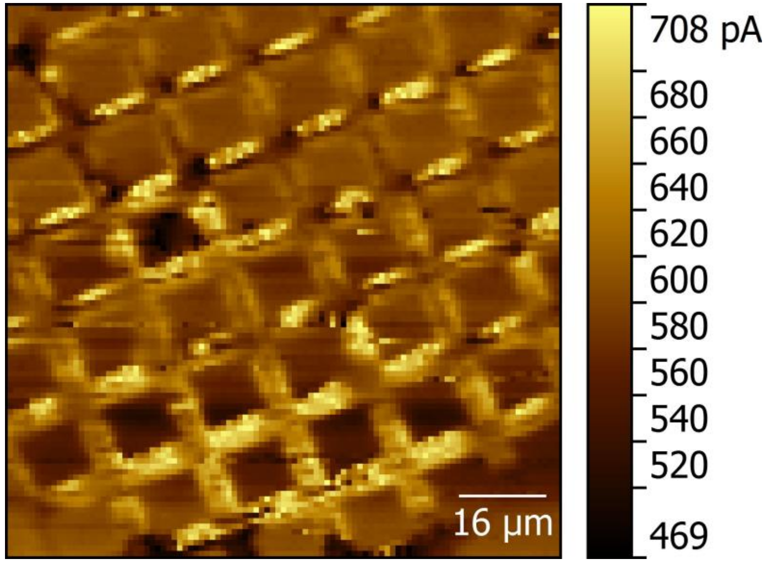
- If the sample is easily coated
- If conductive features are a similar scale to the probe
- To reduce the influence of topography
- To produce/interact with the redox mediator of interest



# Biased sample example.




Biased Sample

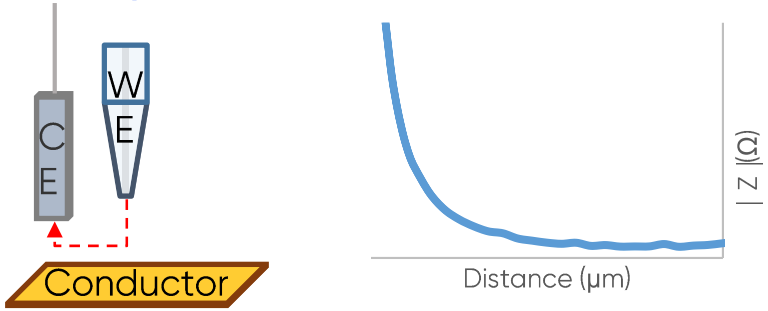



**A TEM Grid made of a mesh of 6 µm Au wire with 10.5 µm holes, was measured in 5 mM $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ in 100 mM KCl solution. SECM measurement was only possible when the TEM substrate was biased at -0.25 V.**

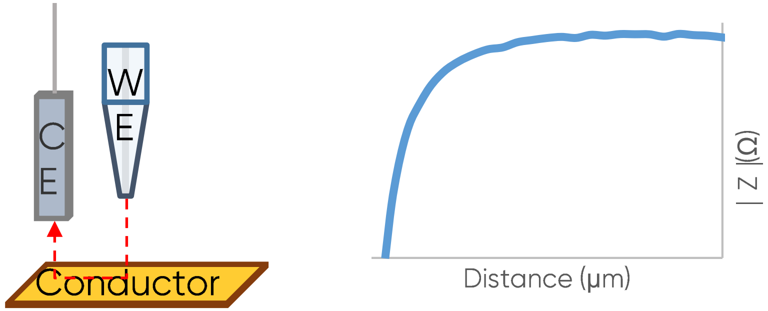
# Considerations in ac-SECM.

# Effect of electrolyte conductivity.

- **Response measured over a conducting region is partly dependent on the electrolyte conductivity**
  - High conductivity electrolyte, for example seawater analogue, causes increase in impedance

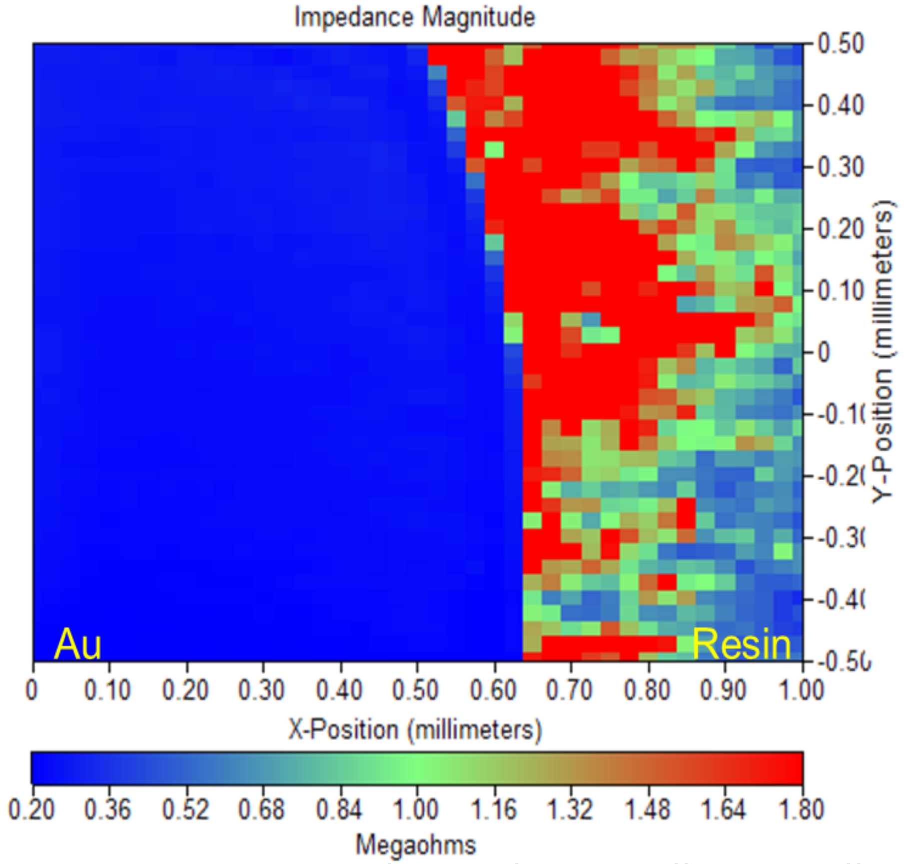



  - Low conductivity electrolyte, for example tap water, causes decrease in impedance

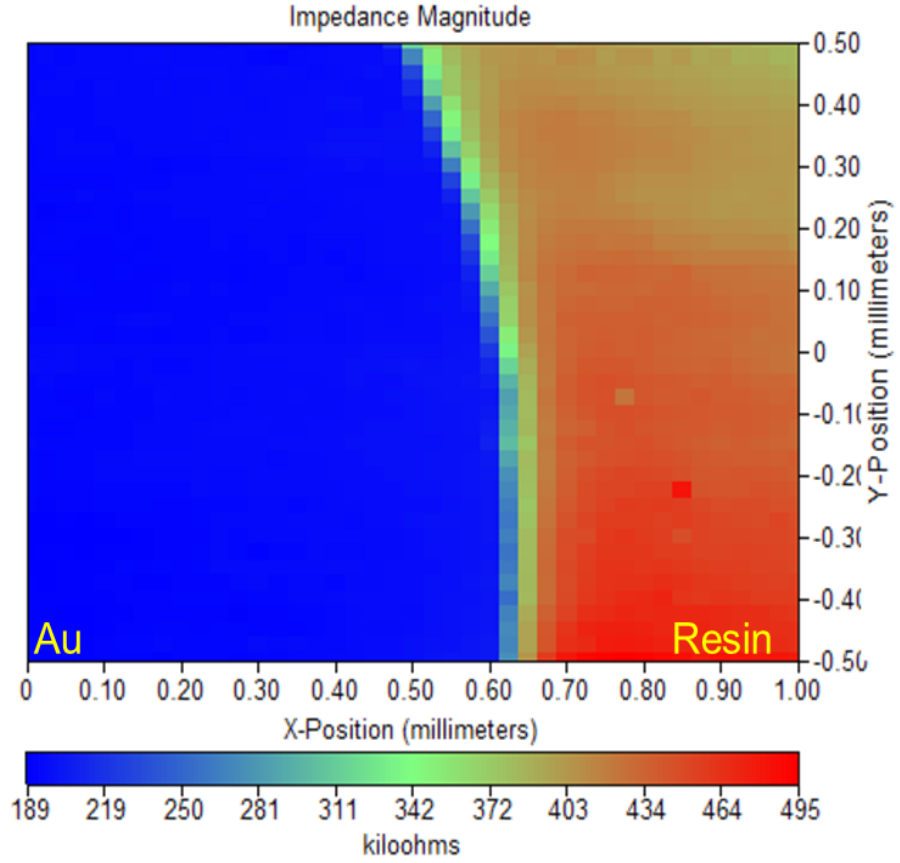


# Deciding on electrolyte.

## High conductivity electrolyte



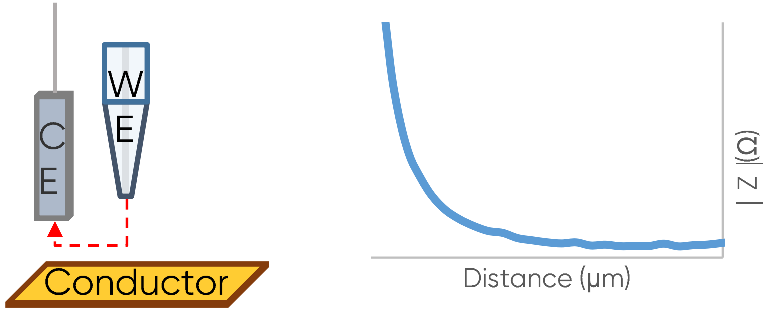

## Low conductivity electrolyte



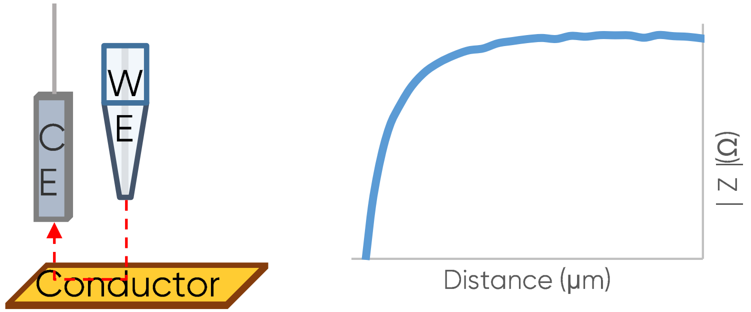

Low conductivity electrolytes will typically give better contrast between conducting and insulating regions. It is still possible to perform measurements in high conductivity electrolyte, and distinguish conducting and insulating regions if a specific electrolyte is of interest.

# Effect of measurement frequency.

- **Response measured over a conducting region is partly dependent on the measurement frequency**
  - Lower frequency causes increase in impedance

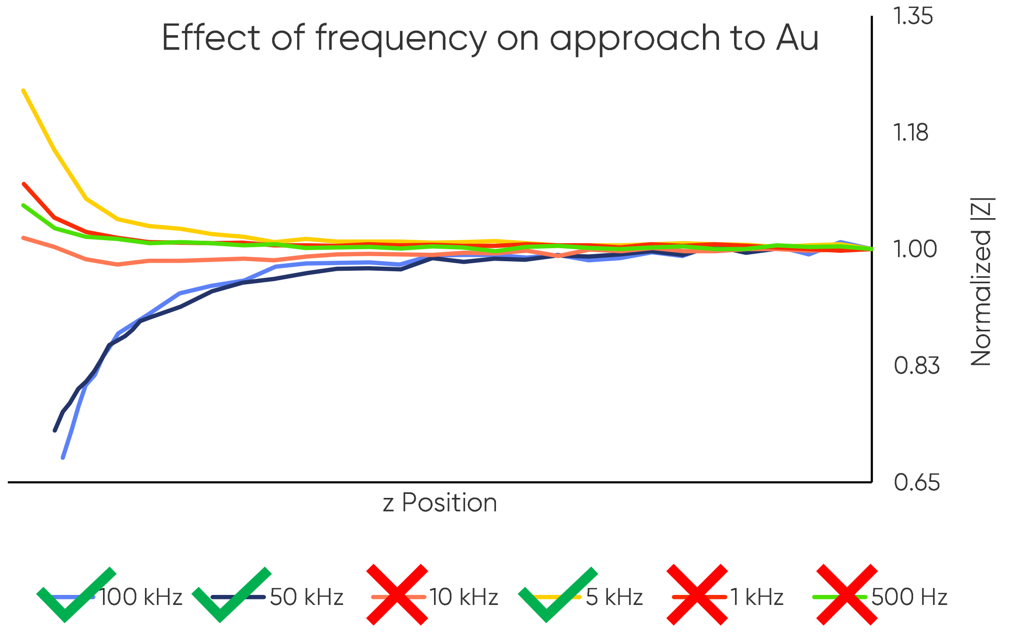



  - Higher frequency causes decrease in impedance



# Deciding on the measurement frequency.

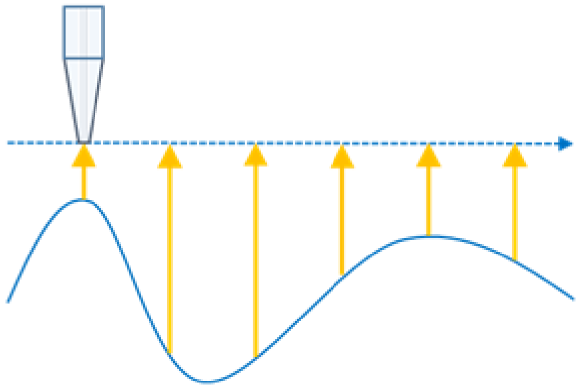
- Higher frequency closely reflects sample activity
- Lower frequency closely reflects sample topography
- For a sharp image the impedance above the sample should be noticeably different from the impedance in bulk solution
- Change in impedance from bulk to final should be gradual



# Constant height or constant distance mode?

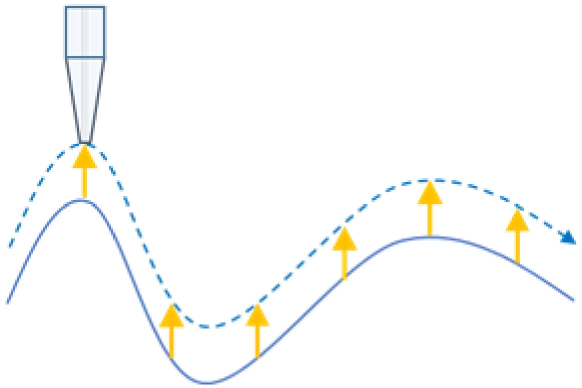
# What is a constant height measurement?

In a constant height measurement the probe is held at a fixed position in z throughout the scan. If there is a change in sample topography a change in probe to sample distance will occur. In SECM changing the probe to sample distance results in a change in the signal measured, therefore the resulting map is influenced by both activity and topography.



# What is a constant distance measurement?

In a constant distance measurement the probe height (z position) changes throughout the measurement to maintain a set probe to sample distance. The probe will follow the topography of the sample. The resulting constant distance measurement is therefore only affected by the sample activity.



# Constant height or constant distance?

## When to use constant height SECM:

- The sample is relatively flat
- There is minimal sample tilt over the measurement range
- Fast measurements are a requirement of the system, e.g. dynamic samples

## When to use constant distance SECM:

- The sample has large changes in topography
- There is large sample tilt over the sample range
- The time scale of the measurement is not a factor

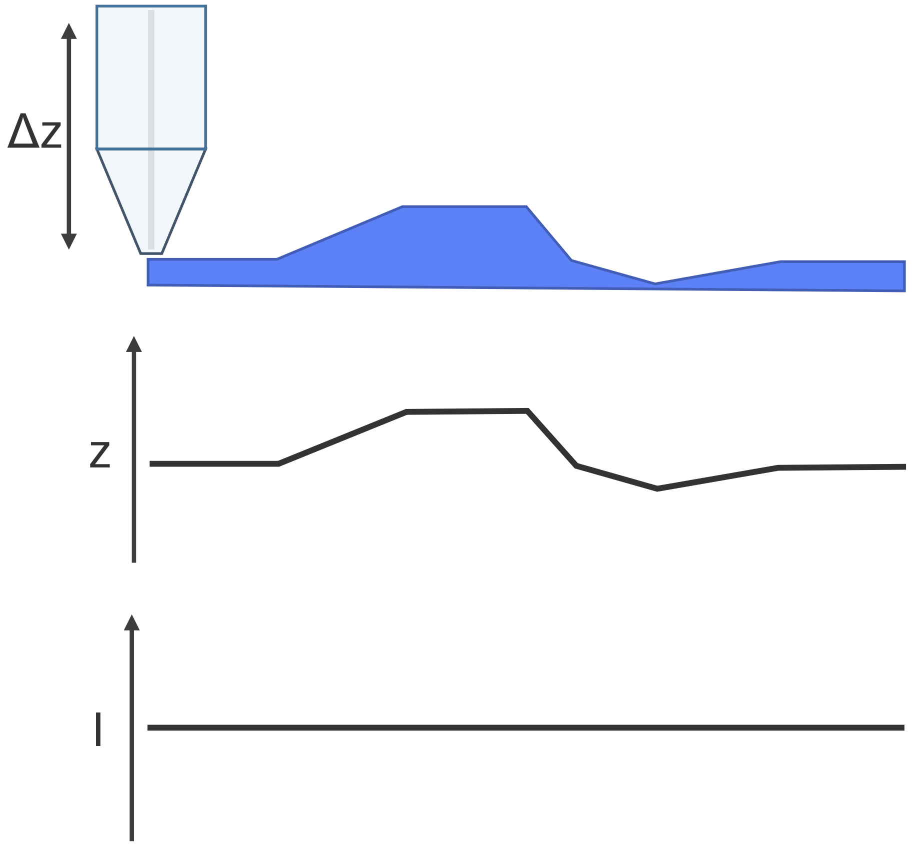
# Following sample topography on the M470

Constant distance measurements can be achieved in one of two ways on the M470:

1. An Optical Surface Profiler (OSP) measurement is first performed to measure topography. The result is then used as an input for a subsequent Height Tracking SECM measurement.
2. Intermittent Contact (ic) – SECM is used to perform a single pass topography and SECM measurement.

# ic-SECM.

# Intermittent Contact – Scanning Electrochemical Microscopy: ic-SECM.

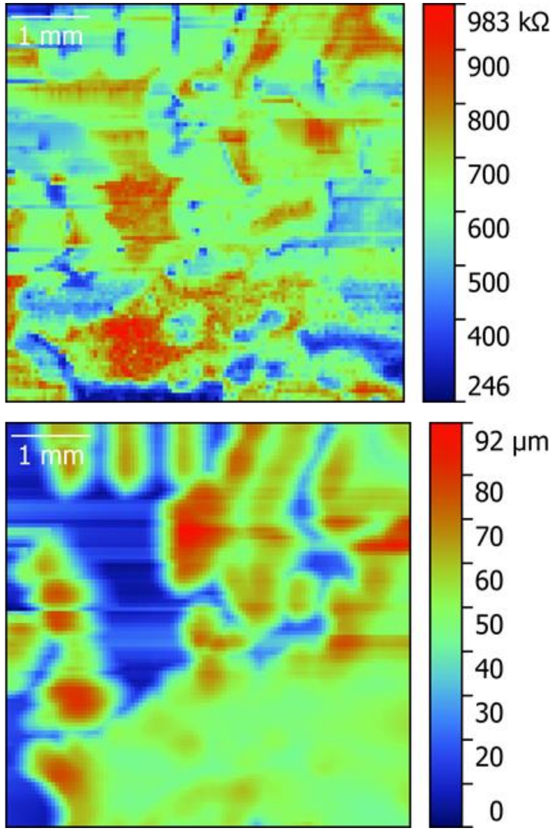



**ic-SECM is performed at a controlled probe to sample distance by vibrating the probe perpendicular to the sample. The probe measures sample activity *and* topography separately in a single measurement.**

**ic-SECM can be used in ac- or dc-SECM mode.**

# When to use ic-SECM.

- **Sample has large topographic changes including:**
  - Surface roughness
  - Curvature
- **Sample tilt over the area of the measurement is difficult to overcome. This is particularly the case for:**
  - Large area scans
  - Samples without large changes in activity




*Impedance (top) and topography (bottom) maps measured on a 20 cent Euro coin using ic-ac-SECM.*

# ic-SECM– Pros & Cons.

## Pros:

- Sample topography and activity are collected allowing for direct correlation
- No need to remove sample tilt prior to measurement
- Approach is performed by the push of a button
- Improved signal due to reduced probe to sample distance

## Cons:

- Not suitable for soft samples
- Requires a longer experiment time

# Conclusion.

# Conclusion.

A number of experimental considerations allow optimisation of the SECM measurement. Understanding how each factor affects the measurement allows users to measure standard and novel samples.

- dc- or ac-SECM?
- Constant height or distance mode?
- For dc-SECM users must consider
  - Experimental mode
  - Redox mediator
- For ac-SECM is performed users must consider
  - Electrolyte
  - Measurement frequency

# More information.

BioLogic Support: https://www.biologic.net/support/

BioLogic Contact: https://www.biologic.net/contact/

# Thank you!

www.biologic.net

contact@biologic.net

BioLogic