Introduction to dc-SECM on the SECM150

Version 1.0

Outline

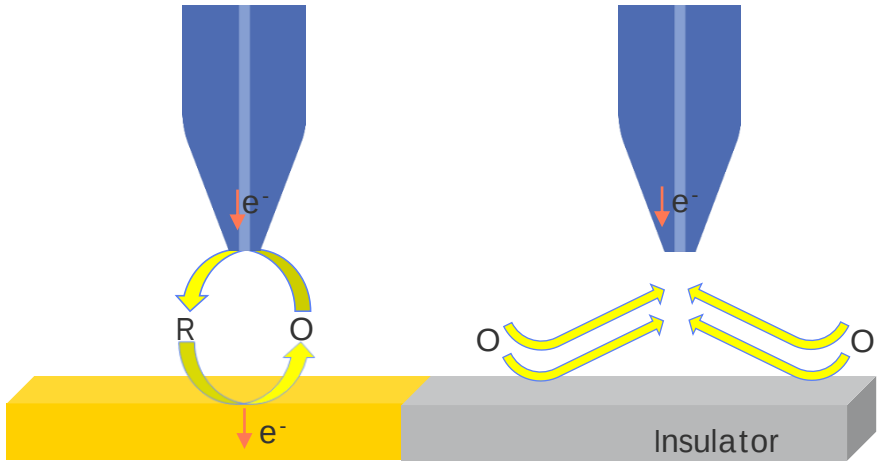
- Introduction to SECM
  - Background
  - dc-SECM Modes
  - Experiment Types
- Introduction to the SECM150
  - Specifications
  - Advantages
  - Applications

Introduction to SECM

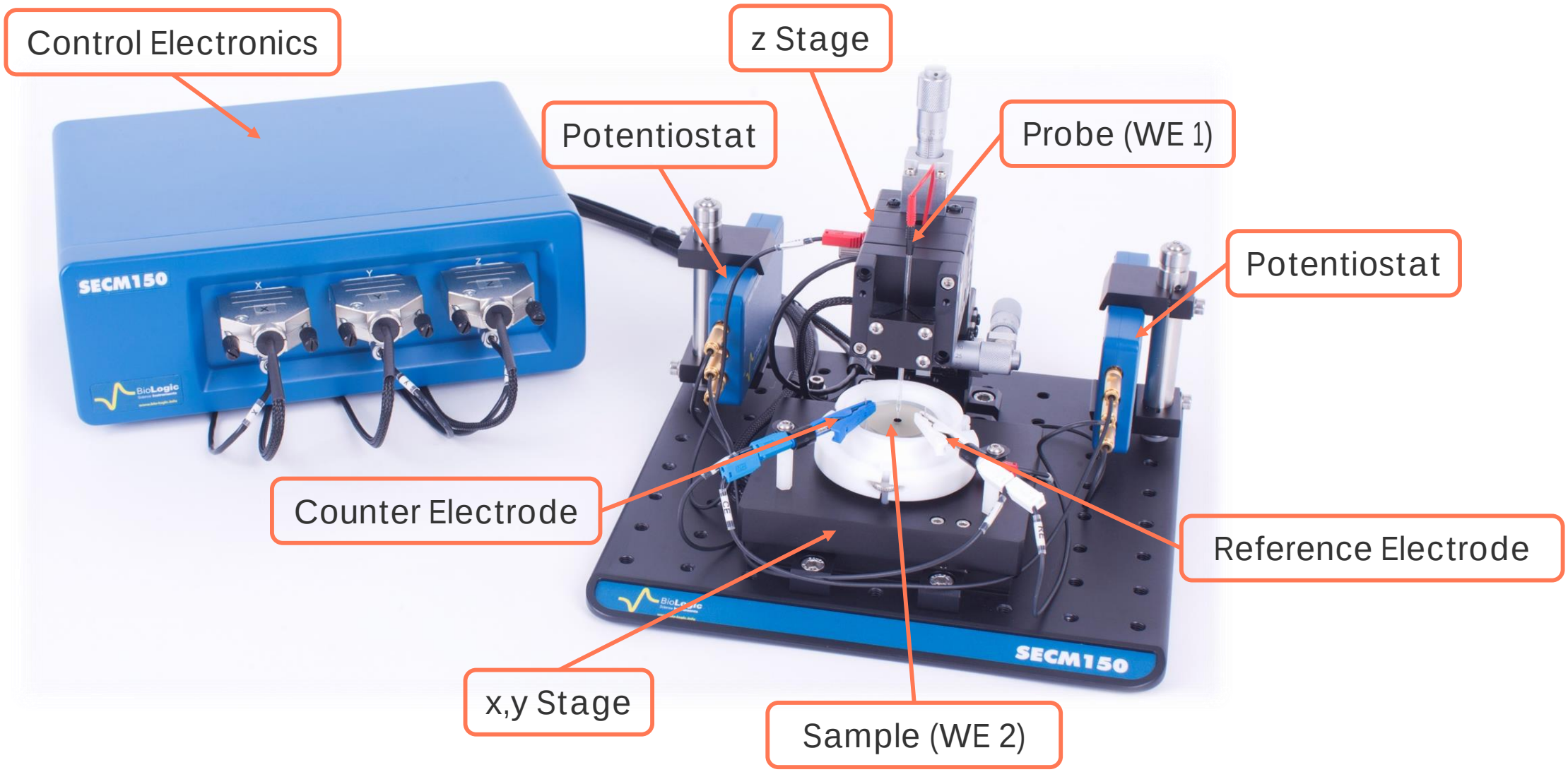
Background

dc-SECM

- Local measure of the electrochemical activity of a sample
- UltraMicroElectrode (UME) probe in close proximity to sample is biased to interact with a redox mediator
- Can be used to produce images with contrast reflecting the reactivity of a surface
- Can be used to investigate reaction kinetics
- Data measured can explain bulk behavior

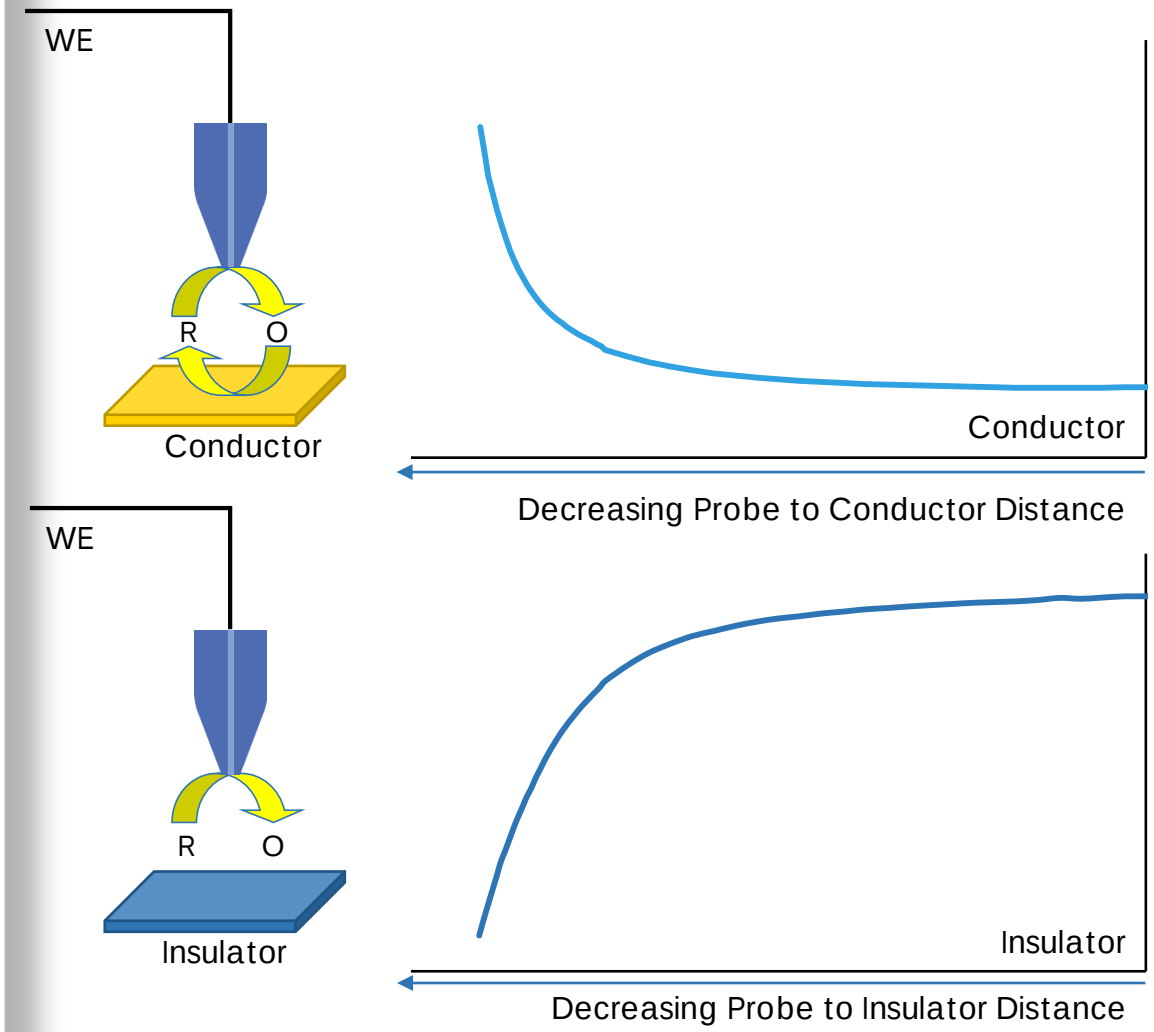


Components of an SECM



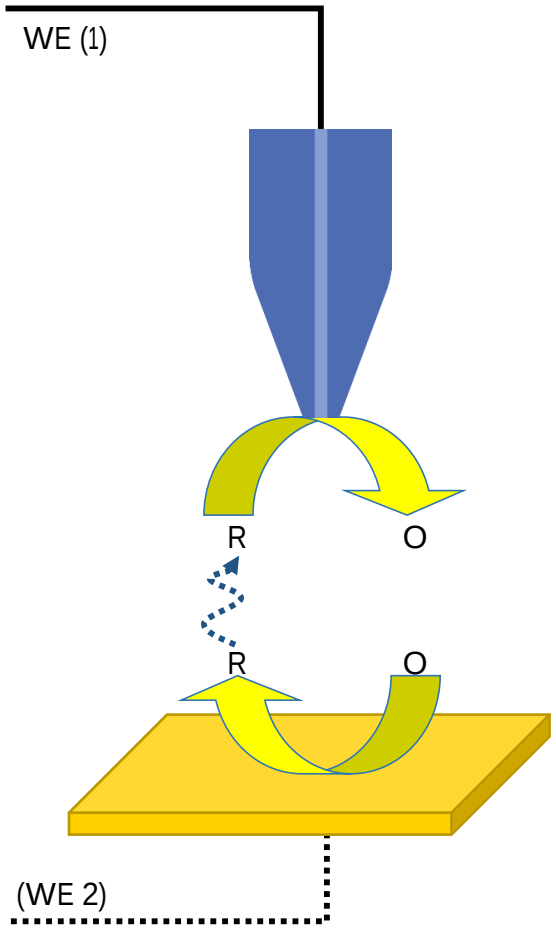
dc-SECM Modes

Feedback (FB) mode



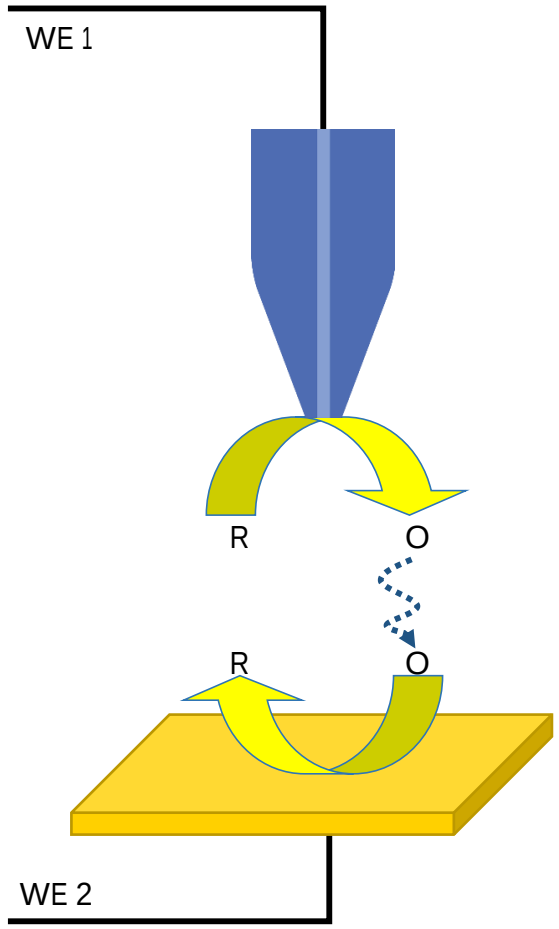
- Most common mode
- Diffusion-controlled current measurement of redox mediator added to solution
- Probe biased to reduce or oxidise the mediator
- Sample remains unbiased
- Increase in current (positive feedback) over conductor
- Decrease in current (negative feedback) over insulator

Substrate Generator/Tip Collector (SG/TC) mode



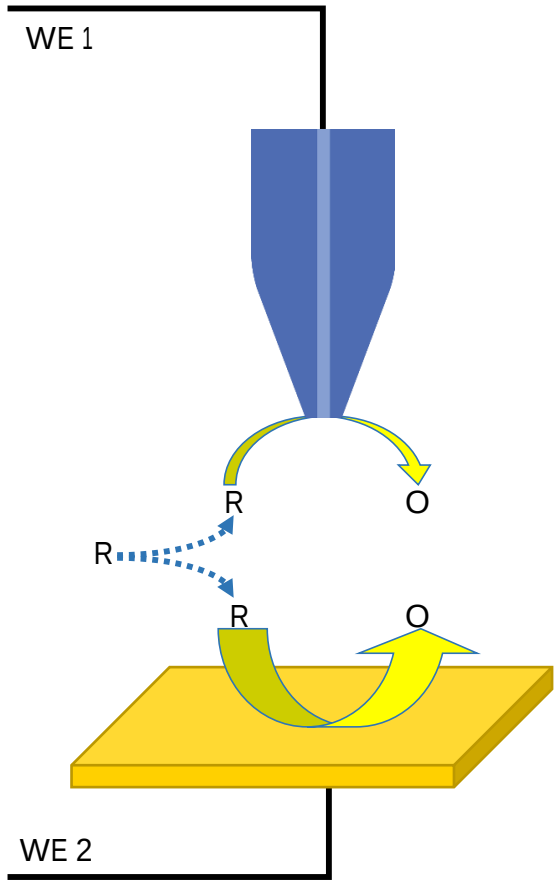
- Substrate *generates* the species which the tip is biased to *collect*
- This species is not originally contained in the solution
- During the measurement the probe moves through the diffusion layer of the generated species at the substrate interface
- The probe is always connected as a working electrode. Depending on the application the sample can act as a second working.

Tip Generator/Substrate Collector (TG/SC) mode



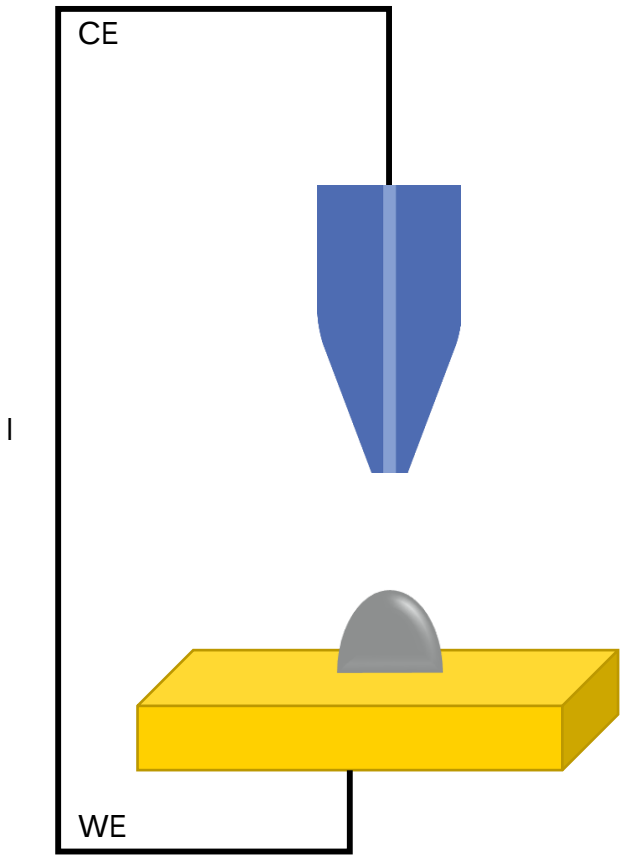
- Tip *generates* the species which the substrate is biased to *collect*
- The generated species may react chemically with the substrate
- The species is not regenerated at the tip
- Typically both the probe and sample are WE
- Tip can be a pipette filled with species of interest

Competition mode



- 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
- When the substrate activity increases a resulting increase in current is detected by the probe

Direct mode

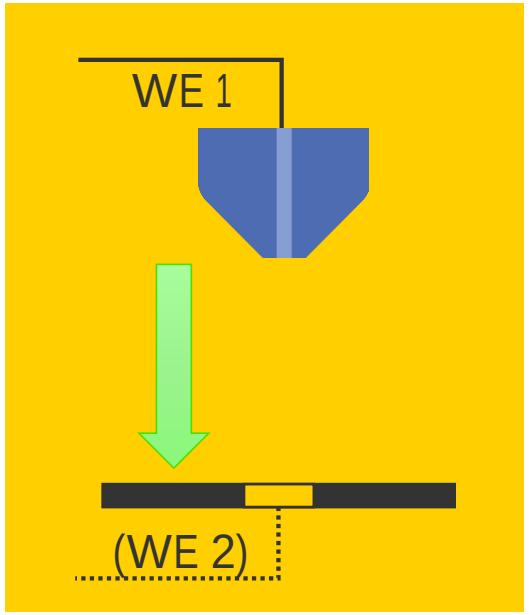


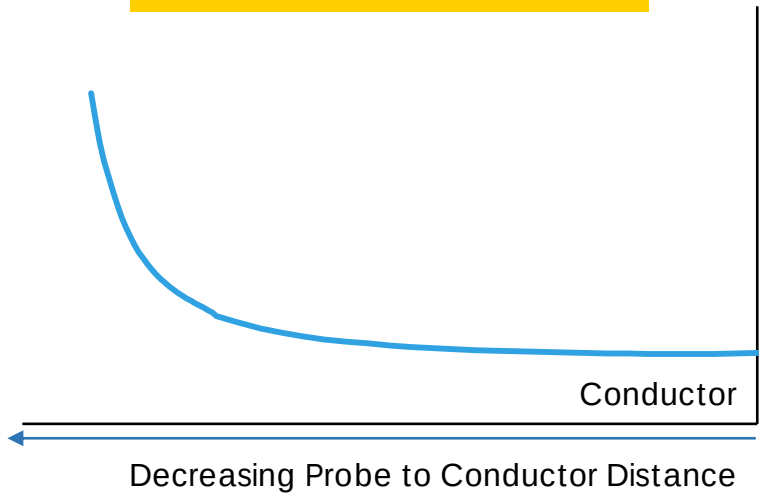
- Three electrode cell with substrate connected as WE and probe as CE
- Localises electric field between probe and sample
- Used for substrate modification including etching, deposition, and patterning.

Experiment Types

Approach curve

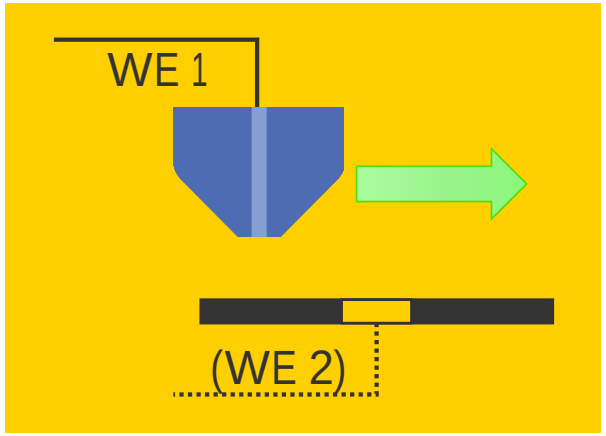
- Used for positioning and stand alone studies
- Signal measured is related to sample activity and probe to sample distance
- Used for quantitative kinetic data for samples hard to study by bulk techniques:
  - Certain interfaces
  - Non-electrochemical substrates: Biological materials
  - Samples difficult to prepare for bulk electrochemistry: 2D materials
- Used to investigate local swelling with time and bias of:
  - Batteries
  - Super capacitors
  - Coatings

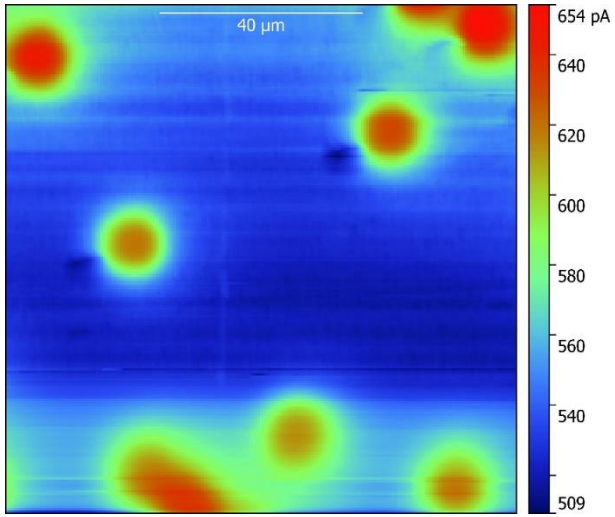




Area Scan

- Raster scanning of probe in close proximity of sample
- Electrochemical heterogeneities are visualized
- Electrochemistry can be correlated with sample features
- Changes to local electrochemical activity can be followed over time

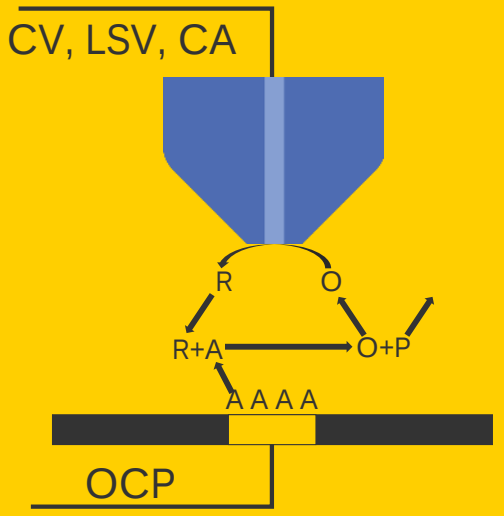




Polycarbonate membrane with 12 µm pores over Au

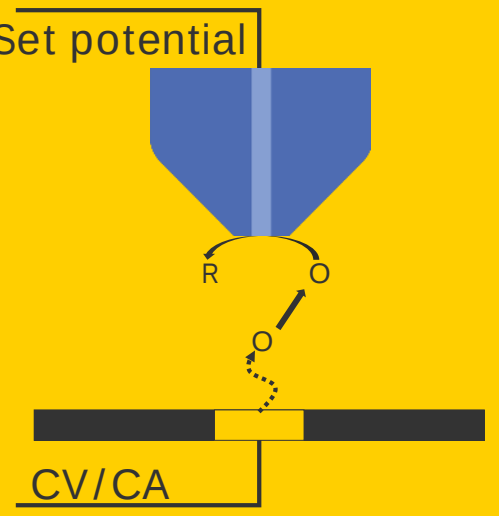
Other

Surface Interrogation (SI)-SECM



- Quantify adsorbed species
- Predominantly used in studies of catalysts
- No complex data treatment required

Tip Substrate Voltammetry (TSV)-SECM



- Information about ion fluxes from adsorption, desorption, and dissolution of species
- Analogous to rotating ring disc electrode
- Used in catalysis and materials

Introduction to the SECM150

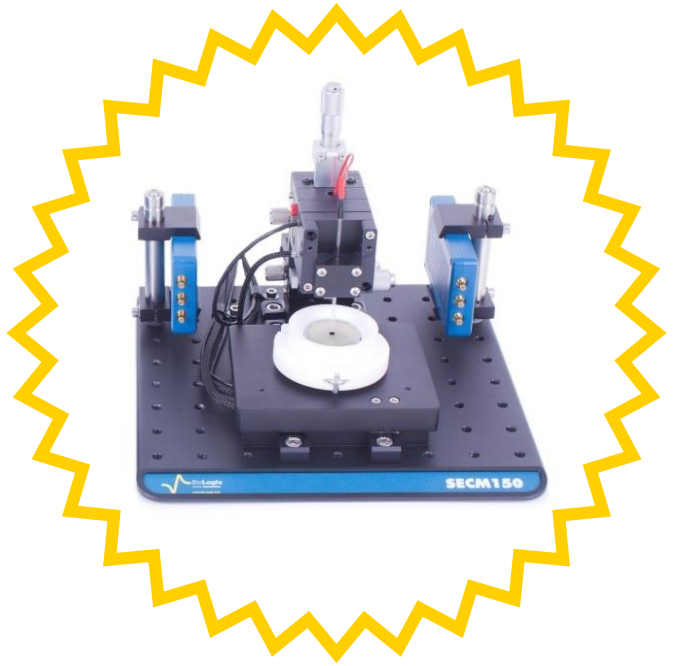
Introduction to the SECM150

- A dc-SECM only instrument suitable for novice and experienced SECM users
- Provided as a complete system, with only a PC required
- **BioLogic's** most compact SECM system
- **BioLogic's** first fully piezo positioned SECM
- Designed for high speed, high resolution measurements

SECM150 the right pick!

Did you know in SECM articles published from start of 2016:

- dc-SECM made up over 95% of publications
- Constant height SECM accounted for over 90% of publications
- Only 5% of dc-SECM publications worked outside of the ±2 V range
- A scan range of 200 µm or less is used in over 50% of publications

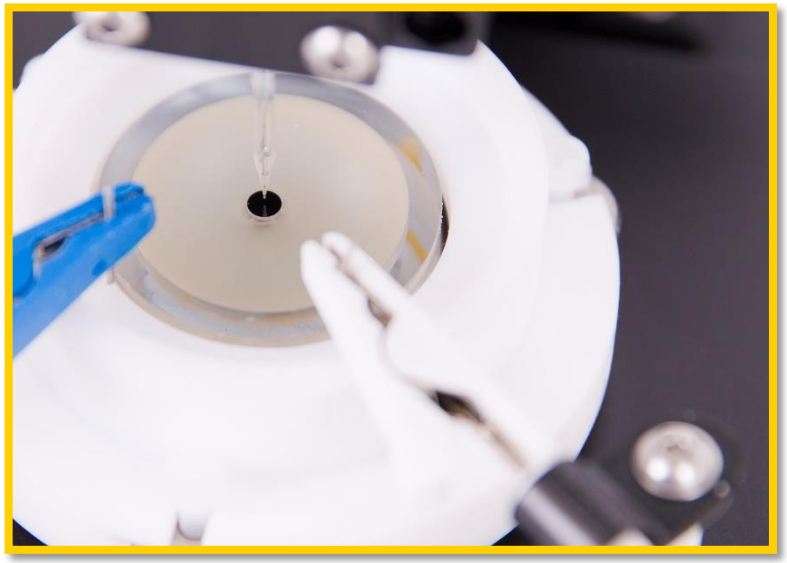


Specifications

General

Dimensions	
Control box	90 x 235 x 180 mm (H x W x D)
Scanning stage	190 x 225 x 230 mm (H x W x D)
Potentiostat	97 x 15 x 54 mm (H x W x D)

Available experiments	
dc-SECM	Approach curve Line scan Area scan
Electrochemistry	Cyclic voltammetry Chronoamperometry Linear voltammetry Chrono OCP

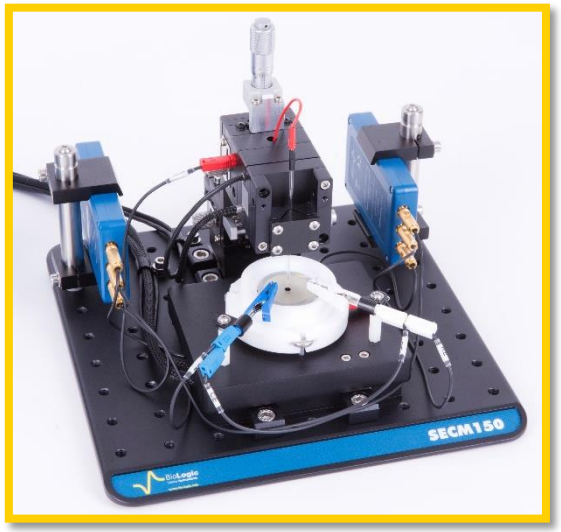


Available probes

1, 2, 5, 10, 15, 25 µm

Scanning Stage

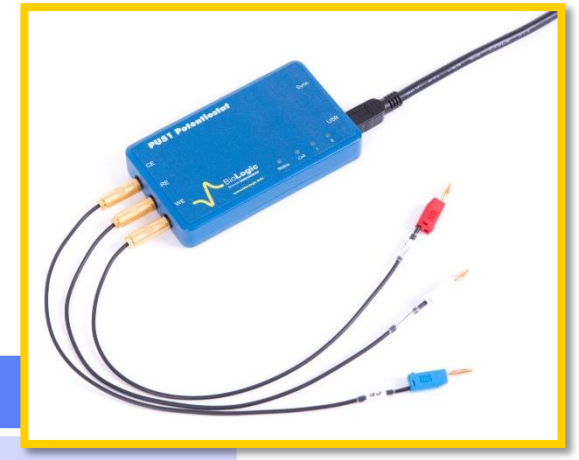
- Automated x, y, z scanning using piezo stages
- Macro positioning using lockable micrometers
- x,y stage decoupled from z stage reducing crosstalk



Positioning Specifications	
Positioning system	Closed –loop piezo stages
Automated scan range	x&y: 200 µm; z: 100 µm
Practical minimum step size	50 nm with <10 nm resolution
Max scan speed	200 µm/s
Max data acquisition for line or area scan	20 points/s
Micrometer macro positioning	13 mm range (min. graduation: 10 µm)

Potentiostats

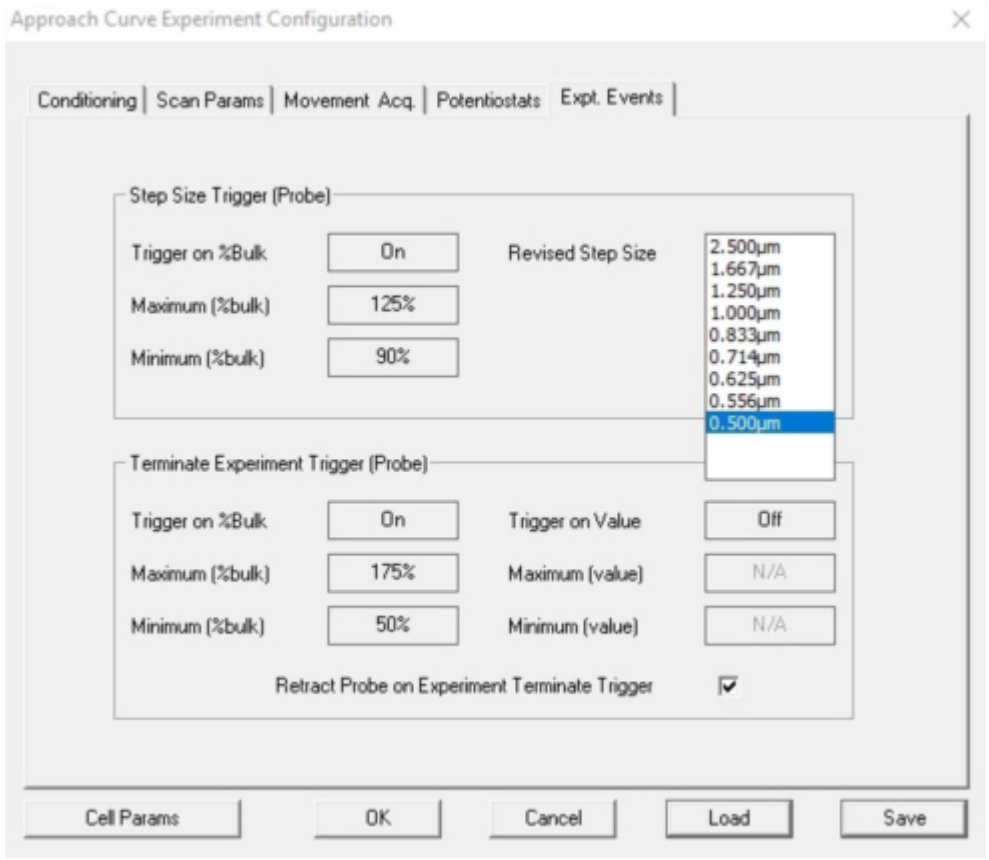
- Uses two compact PU51 potentiostats
- Both potentiostats are controlled from within the experiment configuration



Potentiostat specification	
Mode	Pstat only
Current measurement	2.56 x 1 mA to 100 pA
Potential	±2.048 V for applied & measured voltage
Electrometer	<10 pA input bias current and 10^{11} Ω ll 5 pF input impedance (R/C)
Time base	Typically 100 µs
Sampling rate	1 mHz to 10 kHz
Max. data samples	100000
Electrical isolation	Yes

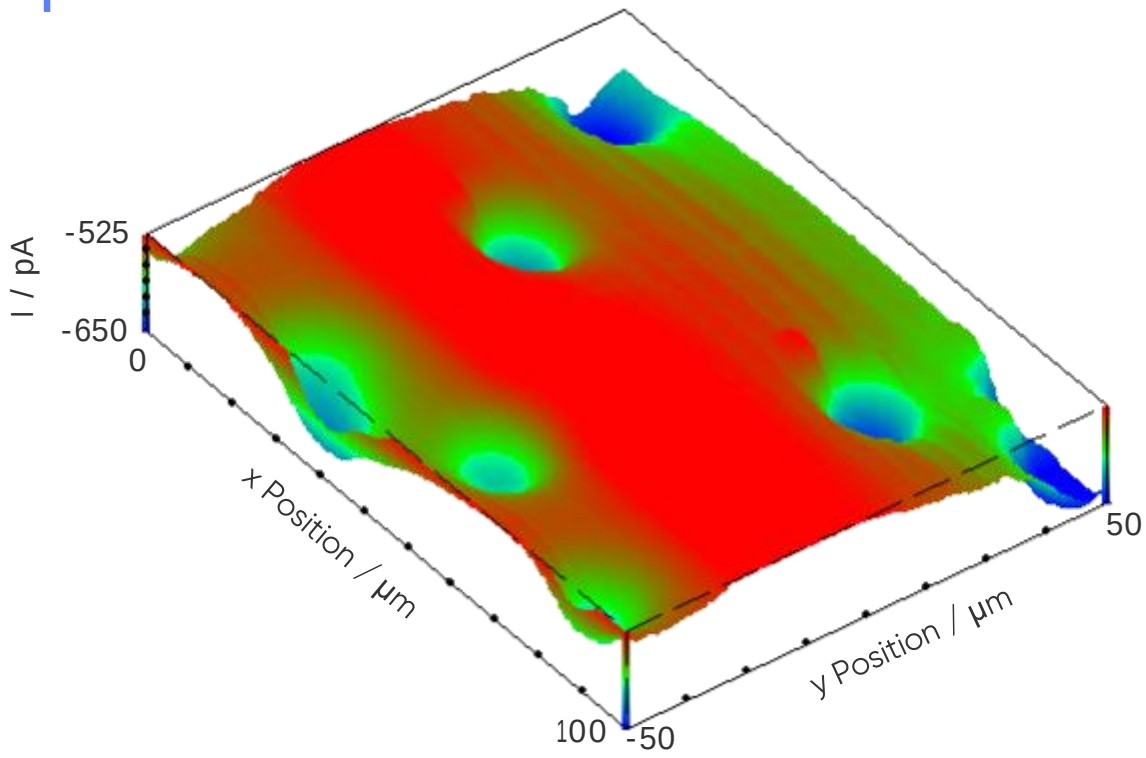
Approach Curves

- Fully automated probe approach curves over entire z piezo range
- Automated triggers can be implemented to:
  - Revise the step size at user defined signal change
  - Terminate the experiment at user defined signal change
- Used for positioning, and substrate characterization



Area Scans

- Fully automated area scans in x,y for local mapping of substrate electrochemical activity
- Can be performed at scan rates up to 200 µm/s, suitable for dynamic samples

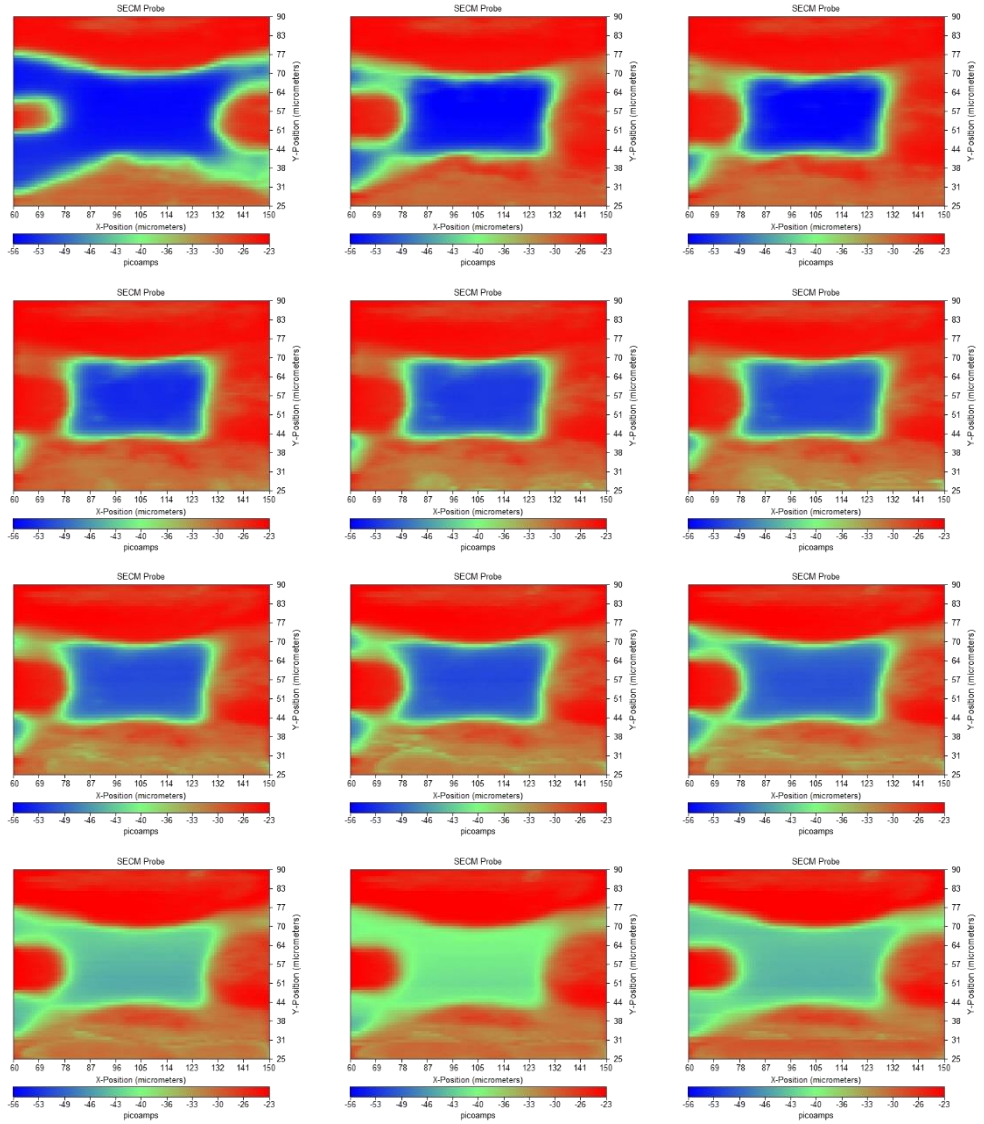


Measurement of polycarbonate membrane with 12 µm pores over Au

Advantages

Scan rate

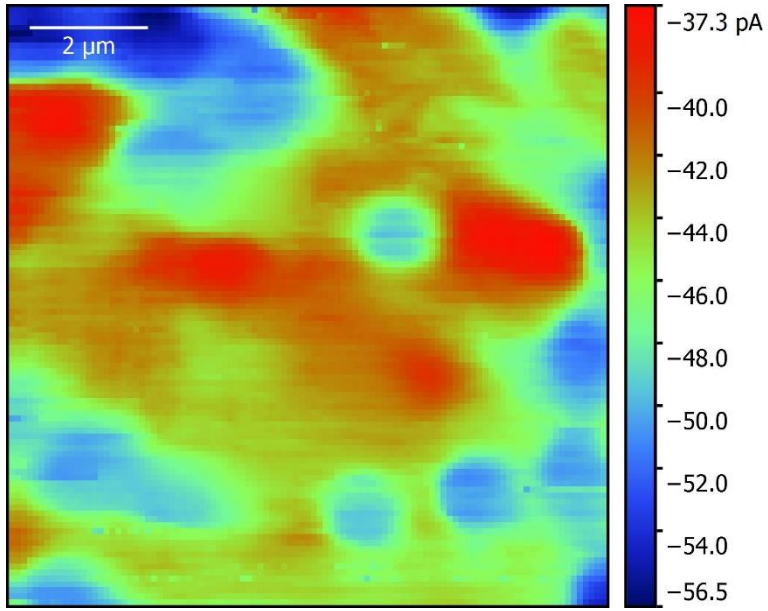
- Faster practical scan speeds than, resulting in shorter experiment times
  - Each experiment on the right took 10.5 min for 91 x 66 points
- Beneficial for investigating fast, dynamic processes
- Beneficial to the study of living cells, which can die with extended scanning periods

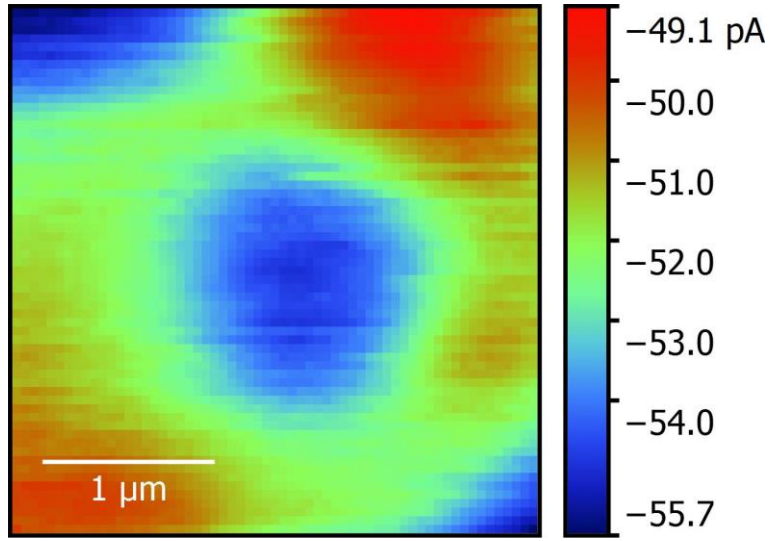


Spider plant stomata after exposure to total darkness measured every ~10.5 minutes

Resolution

- Minimum step size of 50 nm
- Designed for use with **BioLogic's** 1 µm probes

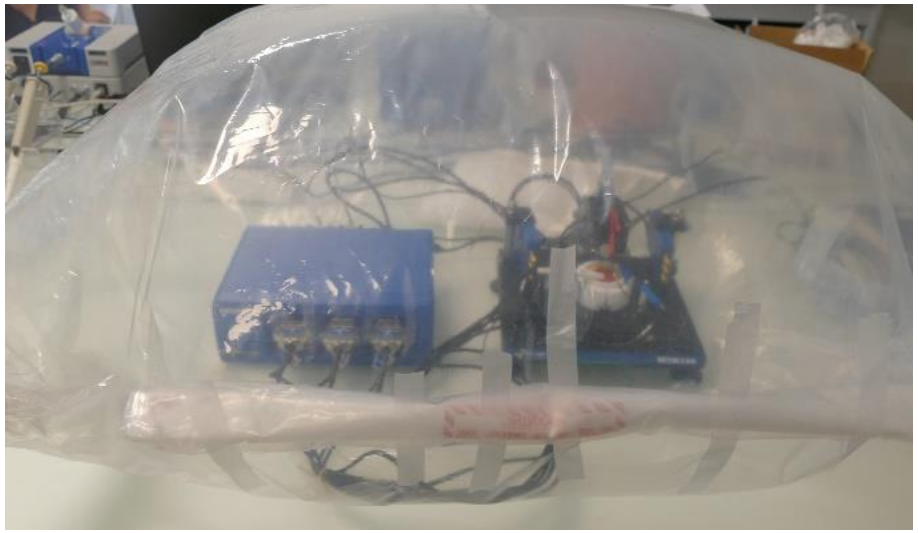


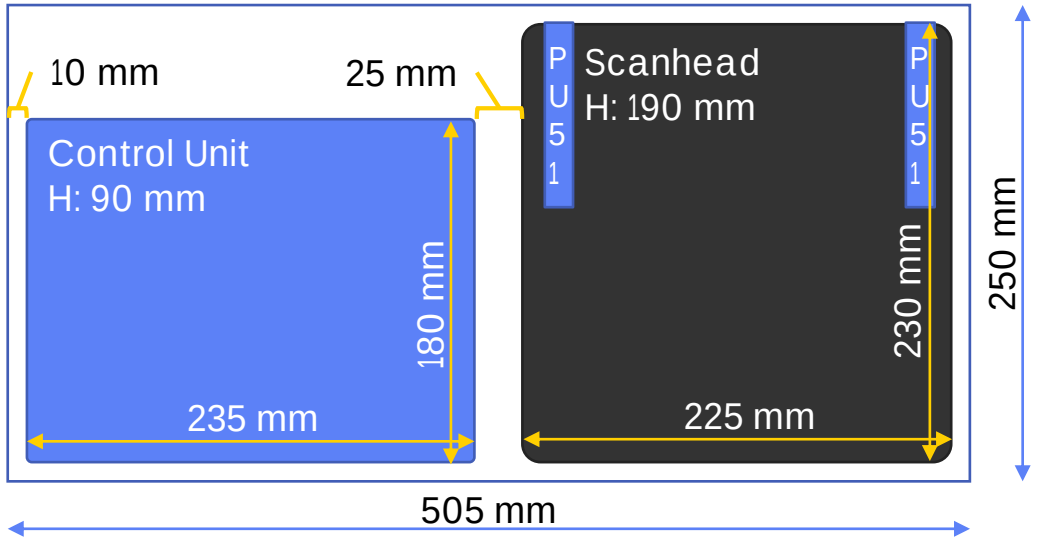


Measurement of polycarbonate membrane with 1 µm pores over Au over 10 x 10 µm² and 3 x 3 µm² areas

Compact size

- The SECM150 was designed to be as compact as possible
- The SECM150 is ideal for applications where space is limited
- The SECM150 has even been demonstrated to fit in an off the shelf glove bag





Applications

What fields is the SECM150 of the most interest to?

- Catalysis

  Example: I. Liberman, W. He, R. Shimoni, R. Ifraemov, I. Hod, Chem. Sci. 11 (2020) 180-185

- Biology

  Example: F. Razzaghi, J. Seguin, A. Amar, S. Griveau, F. Bedioui, Electrochim. Acta 157 (2015) 95-100

- Materials

  Example: T. Bourgeteau, S. Le Vot, M. Bertucchi, V. Derycke, B. Jousselme, S. Campidelli, R. Cornut, J. Phys. Chem. Lett. 5 (2014) 4162−4166

- Corrosion and coatings

  Example: Y. Elkebir, S. Mallarino, D. Trinh, S. Touzain, Electrochim. Acta 337 (2020) 135766

- Green energy

  Example: K. Fic, A. Płatek, J. Piwek, J. Menzel, A. Ślesiński, P. Bujewska, P. Galek, E. Frąckowiak, Energy Storage Mater. 22 (2019) 1-14

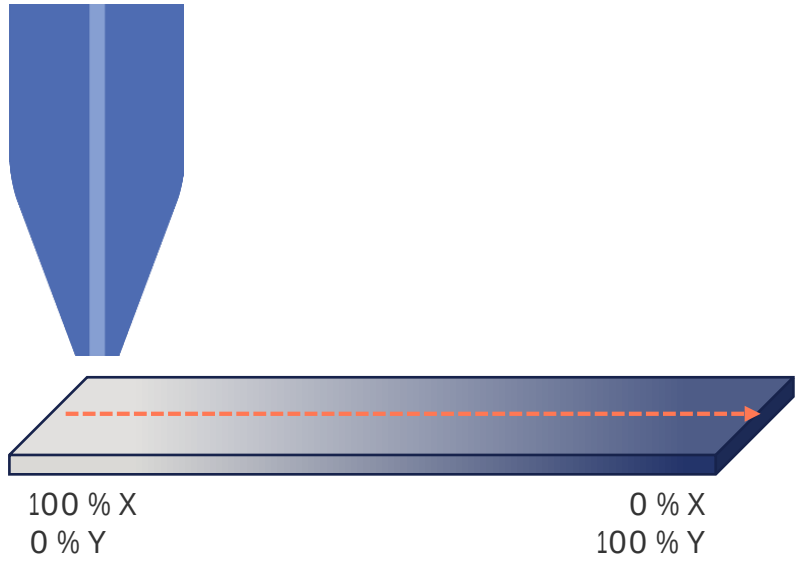
Catalysis

Topics of interest:

- High throughput screening of combinatorial libraries
- Screen individual catalytic materials
- Understand adsorption mechanisms

Requirements:

- *In-situ* screening
- Local assessment
- Chemical selectivity



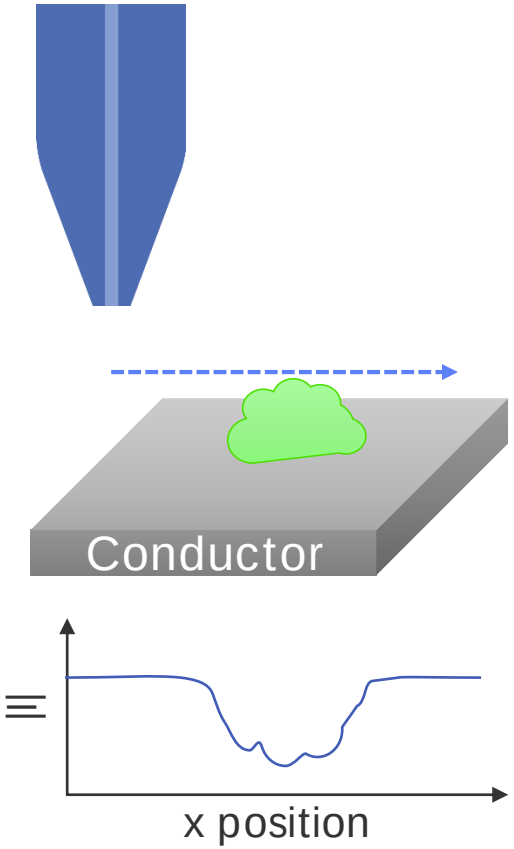
Biology

Topics of interest:

- Investigation of stress on biological systems
- Study ion flow through membranes
- Measure enzymatic activity
- Determine uptake of metabolites

Requirements:

- *In-situ* measurements
- Morphology information
- Chemical selectivity
- Ability to follow system evolution



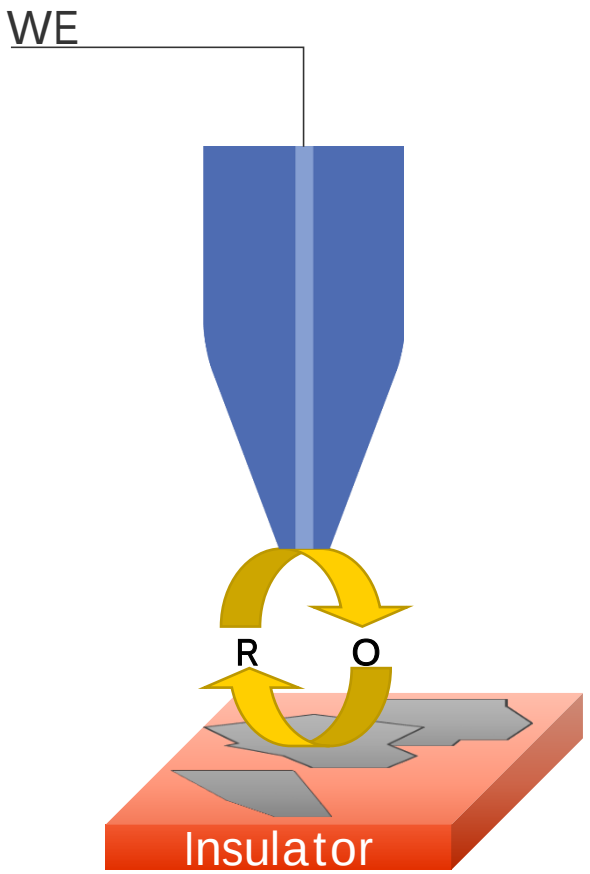
Materials

Topics of interest:

- Study local electronic transport
- Investigate the effect of the local structure of a material
- Perform screening for materials discovery

Requirements:

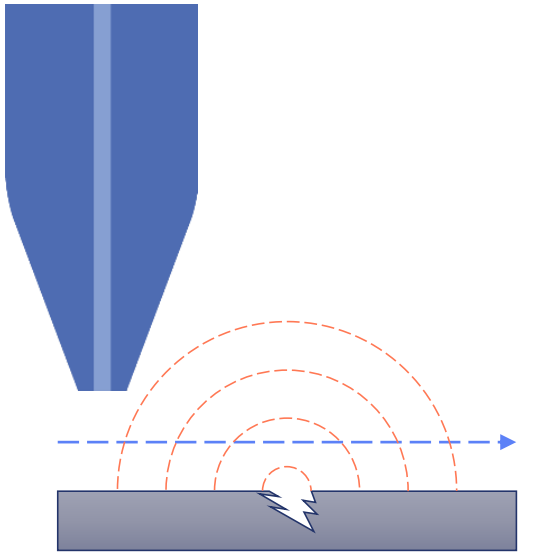
- Local information
- Information about electronic characteristics



Corrosion and Coatings

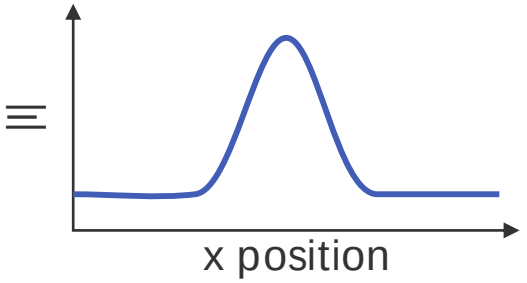
Topics of interest:

- Study coating degradation & failure
- Follow healing of smart coatings
- Determine the effectiveness of corrosion inhibitors
- Follow the evolution of corrosion



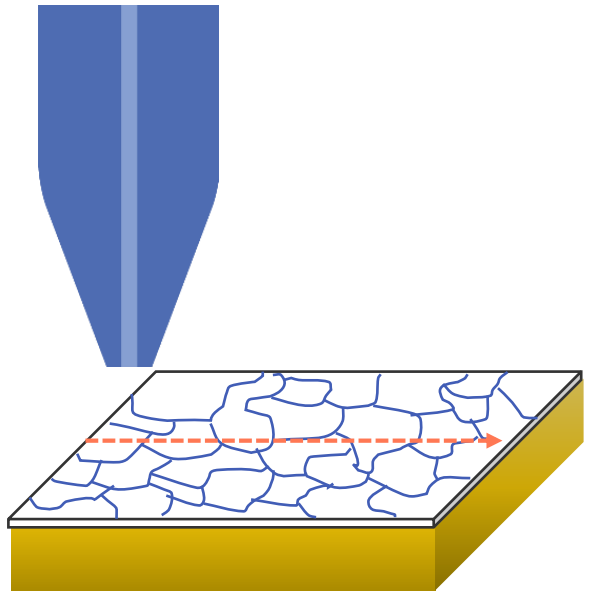
Requirements:

- *In-situ* measurements
- Local information
- Ability to follow system evolution
- Identify variations in activity

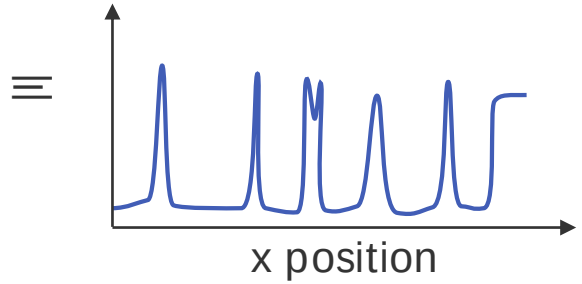


Green Energy

Topics of interest:
- Investigate electrode swelling
- Study the solid electrolyte interface
- Examine fuel cell catalysts
- Screen novel materials



Requirements:
- Local electrochemical information
- *In-situ* measurements
- Non-destructive measurements
- Ability to follow system evolution



Summary

Summary

- The SECM150 is a compact dc-SECM only system designed for high speed, high resolution scanning
- SECM150 is highly applicable to many experiments
- The SECM150 is of interest to catalysis, biology, materials, corrosion and coatings, green energy

BioLogic

Thank you!

www.biologic.net

contact@biologic.net

BioLogic

Resources

dc-SECM resources

Tutorials

- How to get clear images in SECM

Learning Center Articles

- SECM101: An Introduction to Scanning Electrochemical Microscopy

SECM150 resources

Application Notes

- Achieving micron scale measurements using the SECM150
- Investigation of the diffusion of ferricyanide through porous membranes using the SECM150
- Using the SECM150 to Measure an NMC Battery Electrode

Technical Notes

- Using the SECM150 in a Controlled Atmosphere in a Glove Bag

Learning Center Articles

- SECM to form and screen micron scale electrocatalysts