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VersaSCAN™

Electrochemical Scanning Base System Manual

AMETEK

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1. VersaSCAN BASE (VSC-BASE)

This section describes the functions of the VSC-BASE. This is the common workstation component of the VersaSCAN platform. General Installation and Setup, Ethernet Communication, home Routine and Manual Control of the positioning system is covered.

1.1 VSC-BASE Packing List

Table 1. VSC-BASE Packing List

Description	Ametek PN	Quantity (Each)
XYZ Stages Motor Controllers	233776	1
Optical Breadboard	233752	1
Vibration Resistant Feet	233916	4
Stages to Board Mounting		
VersaSCAN Stage Interface Plate	224060	1
Screw M6x12mm	233194	4
Washer M6 Split, 9.9mm OD	233784	4
Washer M6 Flat, 12mm OD	233783	4
Bracket to Stages Mounting		
VersaSCAN Mounting Block	224061	1
Screw M5x0.8-14mm	233785	4
Washer M5 Split, 8.8mm OD	233787	4
Washer M5 Flat, 10mm OD	233786	4
Level		
Level, Bull's Eye 7/8 Dia. Flanged	233865	1
Laptop		
Laptop	224123	1
Communications Cables		
Ethernet Switch, 5-port, 10/100	233794	1
Ethernet Cables	683730	3
Power Cables		
Power Supply, Motion Controller, 24V	1117778	1
Power Cord	233950	2
Extension Cord	803937	2
Outlet Strip IEC320	233948	1
Power Supply, Desktop, 12V 2A	233949	1
Shipping and Documentation		
VersaSCAN Base XYZ Pelican Case	244170	1
VersaSCAN Software	224102	1
VersaSCAN Manual	224213	1

NOTE Internal mounting hardware, such as screws, etc. are not included in this packing list.

1.2 VersaSCAN Initial Assembly and Set-up

The VersaSCAN ships with the XYZ Positioning Stages assembled.

Mount the 4 Vibration Resistant feet to the Optical Base. By mounting this first, users can easily lift the base for feet installation without worrying about sliding the stages. From there, follow the instructions on the drawing below to help assemble the XYZ Positioning Stages to the Optical Base. Mounting the stages to the base will require a 5mm Allen Wrench.

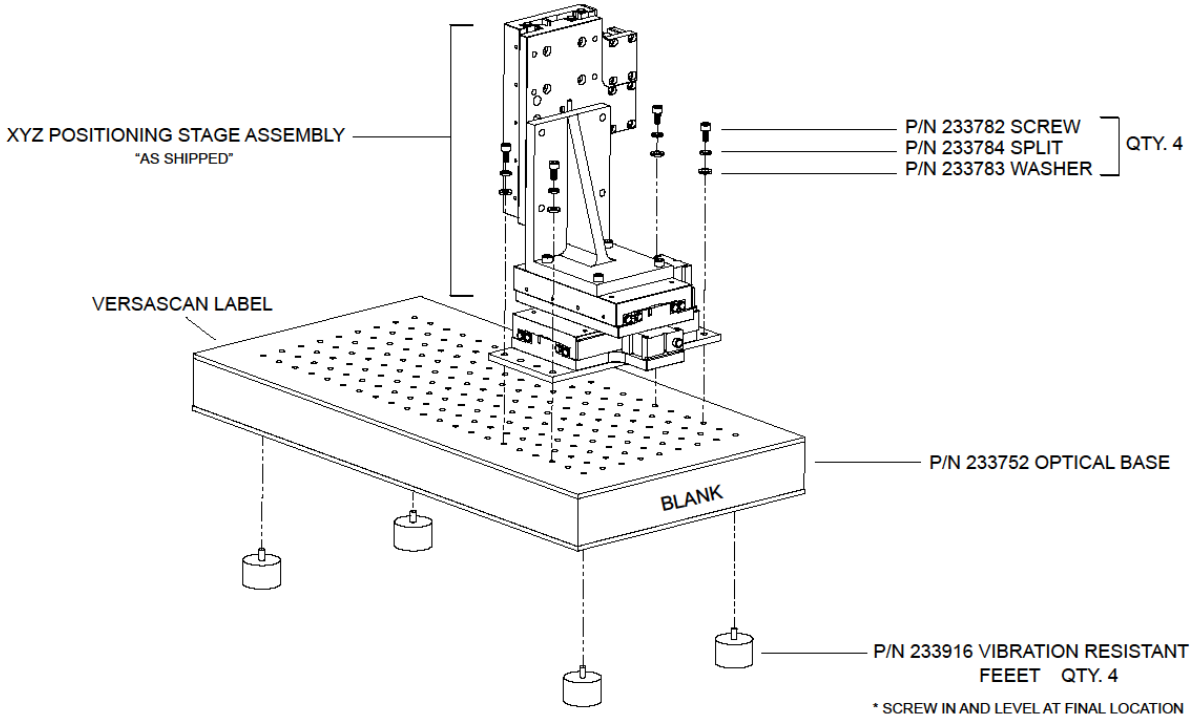


Figure 1. Mount Stage Assembly

Use the bubble level provided to level the optical base.

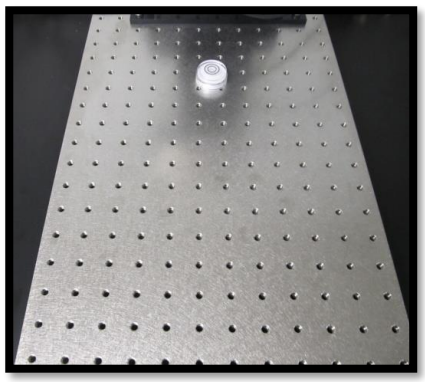


Figure 2. Bubble Level

Take this opportunity to position and mount the supplied Interface Block to the Z Stage with the

following instructions.

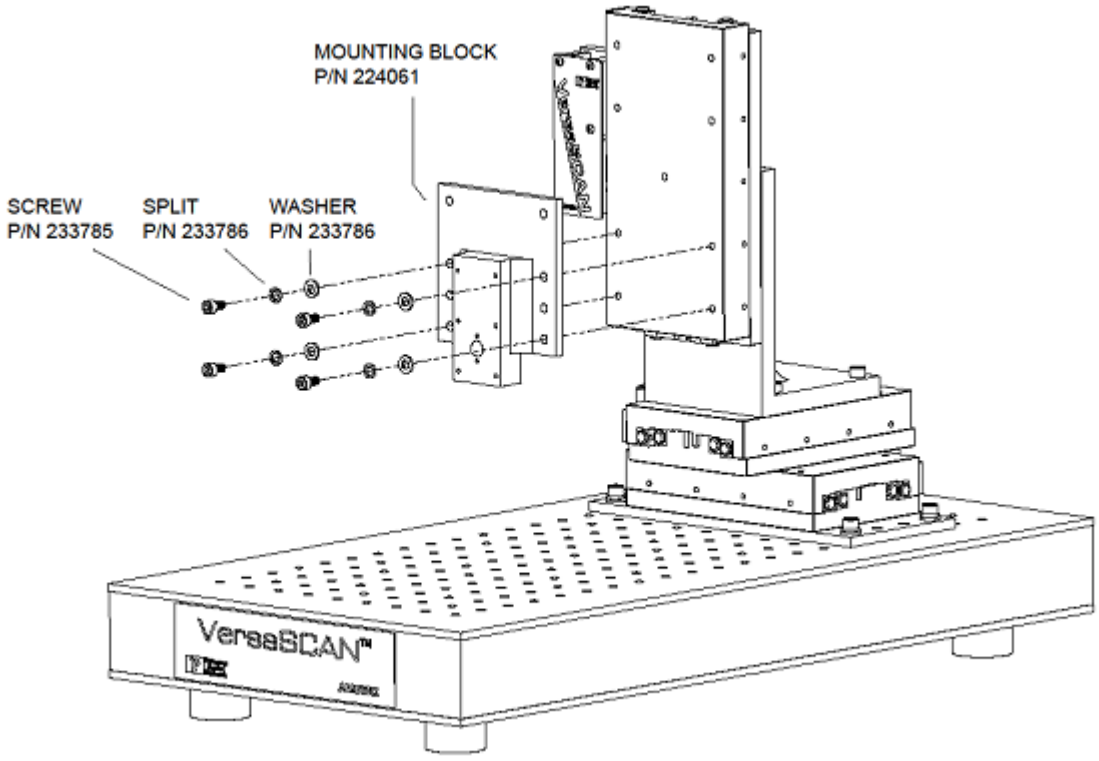


Figure 3. Mounting Interface Block to Assembly

Connect the 6 cables from the Stages to the Motion Controllers.

> **NOTE** Each axis has one cable to command the stage and one cable to read from the linear encoder. These are labeled “X” or “Y” or “Z” and mount to either “Motor” or “Encoder”. Note to ensure that the encoder does connect to “Encoder” and not “S/C Encoder”. The difference in Motor and Encoder cables are easily identified as they will not mount incorrectly.

1.3 Axis Lockers

In shipment, the stages are locked into position with an Axis Locker on each stage.

It is crucial that **all 3** of these are removed before the stages are moved. Take this opportunity to remove them now with a Philips head screwdriver. Store the Axis Lockers as these will be needed if the system is ever transported to a new location.

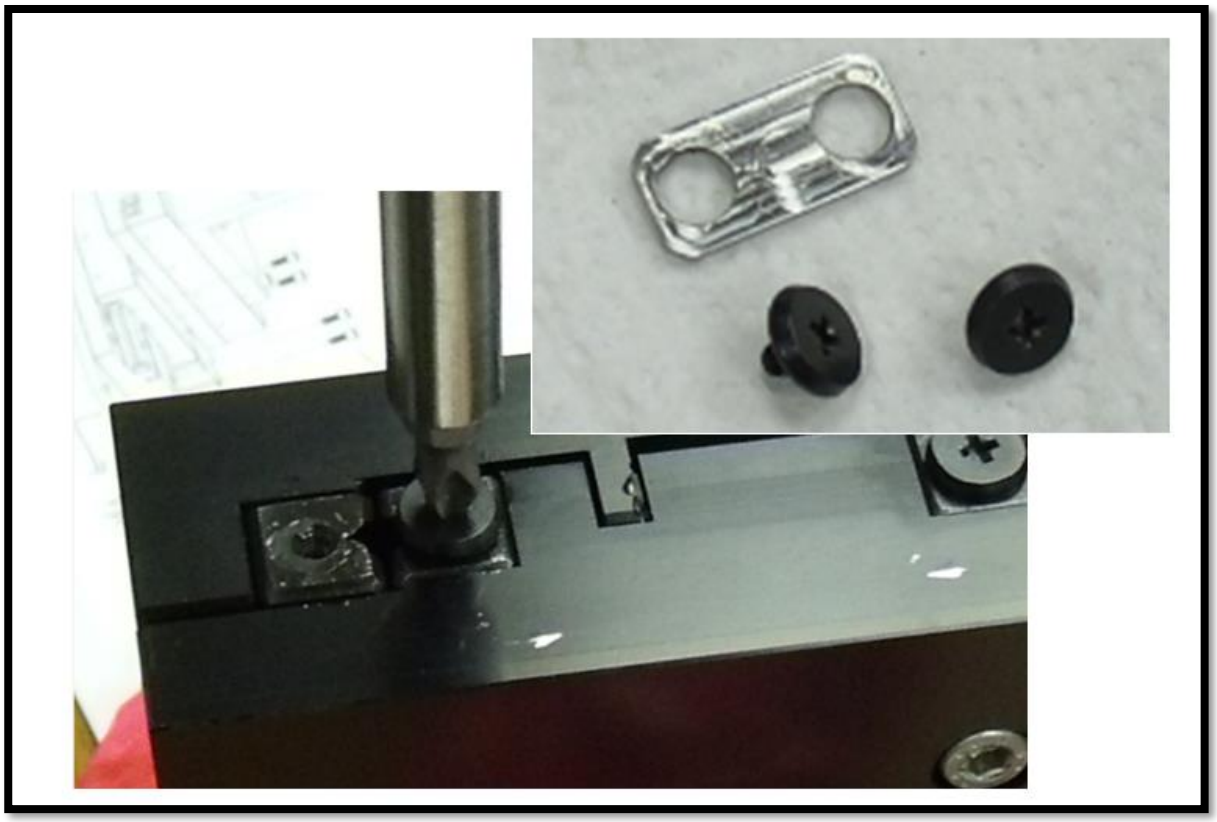


Figure 4. Axis Lockers

1.4 Connectivity and Setting the IP Addresses

All IP Addresses should be set at the factory. The VersaSCAN software will look for these specific devices on these addresses, so these are required for proper communication.

For reference the default IP Addresses are:

Table 2. Default IP Addresses

XYZ Controller	192.168.10.11	Supplied with VSC-BASE
Lock-in Amplifier	192.168.10.9	Supplied with VSC-SVET, VSC-SKP
Laser Profiler	192.168.10.10	Supplied with VSC-OSP
Pstat 1	USB Connection	Drivers installed through VersaStudio software package, supplied with VSC-SECM, VSC-SDC
Pstat 2	USB Connection	Drivers installed through VersaStudio software package, supplied with VSC-SECM, VSC-SDC
Computer	The CPU needs to be set to the same local network as the other components. This is the 192.168.10.X setting where "X" is a numeric value that is different to all other computers and devices, e.g., 192.168.10.100.	

NOTE If the system has TWO motion controller boxes, please refer to Appendix 1 for set-up diagrams.

Setting the IP Addresses is beyond the scope of this document, but Ametek's Technical Support staff can assist as needed.

All Ethernet devices should be connected to the supplied Ethernet hub.

All potentiostats should be connected to the USB ports on the computer.

1.5 Getting Started and Home Routine

Separate documents fully describe the functions of the software and describe the data file structure, Projects, Experiments, Steps, etc.

When the power is turned off to the controllers, they lose their knowledge of absolute position. When this happens a Home Routine needs to be performed, so that the controllers validate their current position and the limits on the scan parameters.

Users will see a message such as this:

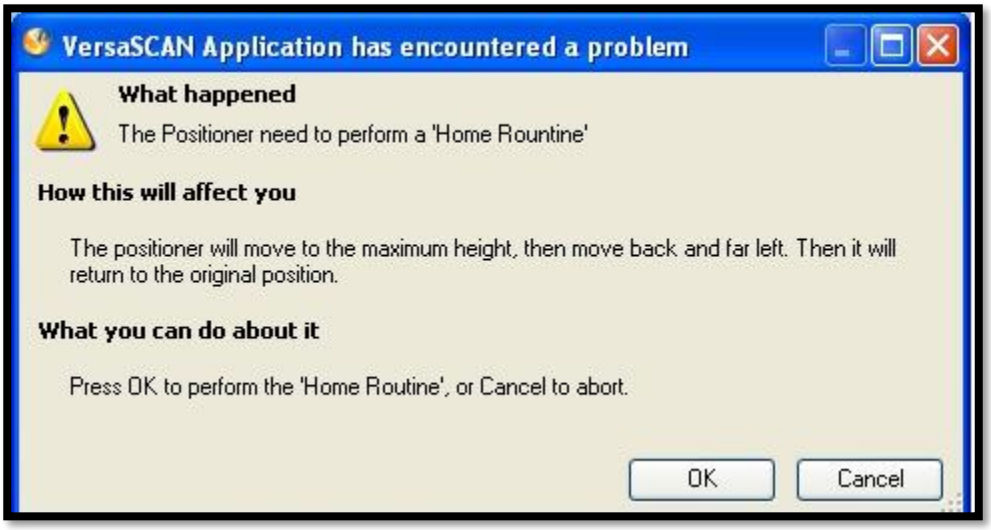


Figure 5. VersaSCAN Warning Message

By acknowledging this message (clicking **OK** button) users command the positioning system to drive the stages to the extreme value. This is to its limit to the left (-X); and back (-Y); and up (+Z). It uses this position as it is the most likely not to create physical contact with samples, cells, or cables such as those between the SECM probe and cell etc. However, please consider that the travel on these stages is 100 mm x 100 mm x 100 mm; so please ensure there is proper clearance prior to running this Home Routine.

Users can also **Cancel** the Home Routine and remove possible obstructions before commencing the Home Routine.

Also, consider this is only required when the Motion Controllers are powered off. If they are left in the Powered (on) state; the system maintains its knowledge of the axial positions and will not need to perform another Home Routine.

After the system finds these absolute limits, it will return to the position where the Home Routine started. It is now ready for experiments or other manual control.

1.6 Manual Control

To enable the Manual Control function, click the **Manual Control** button on the top right of the home screen.

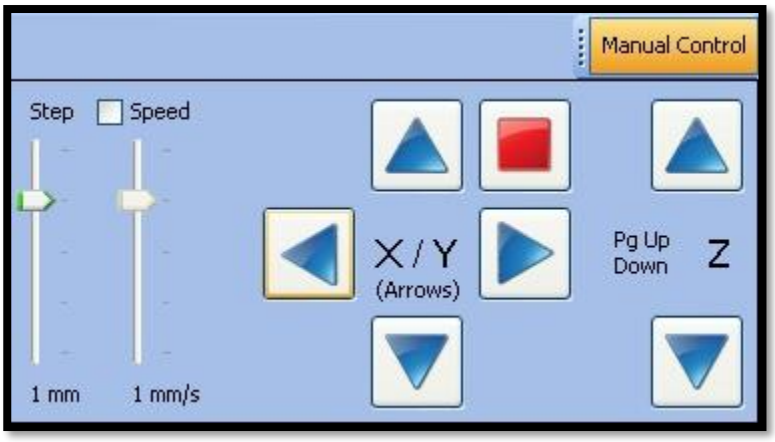


Figure 6. Home Screen

Using this window, users can drive the stages to a given position by either using the mouse to click on the directional arrows or using the keypad for the designated movements. **It is important to consider the speed at which the probe will move when one of these directional movements is activated.**

The Step (distance) and Speed are set using the sliding bar on the left.

Users can use the check box to enable these to be locked in step. Therefore, 1 click moves the distance of 1 step at the given distance. Or these can be independently set.

It is highly recommended that users familiarize themselves with the mechanics of this Manual Control before mounting a probe to the system. Users can see how fast the different movements are and the response time required as the probe moves.

Generally, the user gradually decreases the Step and Speed as the probe approaches the sample. The slide-bar makes it easy to reduce the Step from e.g., 1 mm → 100 µm → 10 µm → 1 µm. This is a typical progression for these movements. Note that the piezoelectric motors produce a more audible sound at lower speeds.

1.7 Probe Position and Experiment Status

This Status Bar displays the active step in the Experiment, here labeled as “Idle”.



Figure 7. Status Bar

The Time section gives a real-time value of the duration of the current Step in the Experiment. Additionally, this window displays the Absolute Position of X and Y and Z in millimeters (mm).

This document describes the framework of the VersaSCAN software. Details on creating projects and experiments for handling data acquisition as well as graphs for data presentation are provided. An accompanying document provides specific information on hardware set-up and specifics of each technique.

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2. VersaSCAN SECM (VSC-SECM)

The VersaSCAN SECM is a Scanning Electrochemical Microscope (SECM). It requires VSC-BASE and VSC-SECM. It is recommended to use VSC-MLCELL and VSC-CAM.

2.1 SECM Technique Overview and Introduction

In a traditional electrochemical measurement, a potentiostat measures an average current over the entire electrode/electrolyte interface. Rarely is a sample homogenous. Samples often consist of local sites of passivate/active nature or sites of anodic/cathodic character. This is needed to investigate localized electrochemistry that led to the development of the Scanning Electrochemical Microscope (SECM).

The SECM integrates a positioning system, a bipotentiostat, and an ultramicroelectrode tip. The positioning system moves the tip close to the surface of the sample. The bipotentiostat polarizes both the sample and the tip independently and measures both resulting currents. The tip is an ultramicroelectrode with a specific tapered polish and active radius lower than 100 microns. The positioning system scans the measurement tip and charts position with measured electrochemical parameters, creating a data map of local current.

One SECM experiment is the Approach Curve in Feedback Mode. In this experiment, a redox active salt, the mediator, is introduced into the electrolyte. A single potentiostat polarizes the tip to cause an electrochemical reaction; however, the sample itself is not polarized. The resulting current is recorded as the tip is incremented towards the sample. When the tip is appropriately close to the sample, a local response is seen. If the location on the sample is conductive, the Nernstian response of the sample causes an increase in current when compared to the bulk current. This is called ‘positive feedback’. If the location on the sample is insulating, mass transport to the electrode of the tip is hindered and a decrease in current is observed when compared to the bulk current. This is called ‘negative feedback’. Intermediate behaviors may occur above different samples. Quantitative analysis of such approach curves allows very accurate local surface kinetics analysis.

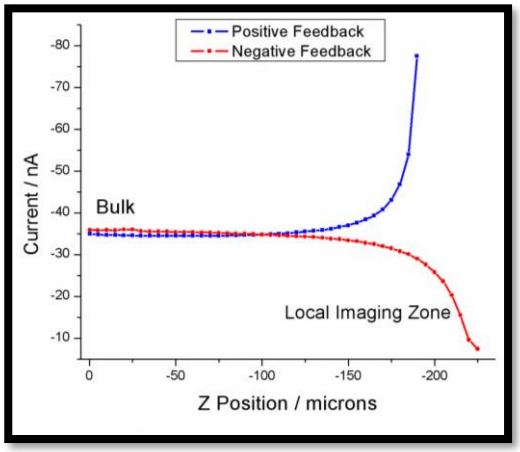


Figure 8. Approach Curve

For imaging experiments, the same kind of approach curve is also used in order to position the tip in the local imaging zone of the sample, without contacting it. The tip-to-sample distance is typically 2 to 4 times the probe diameter for surface imaging experiments. Considering that the tip is 10s of microns, a non-visual means to identify this zone is important.

In Generator-Collector mode, the SECM uses the second channel of the bipotentiostat to polarize the sample and actively control the redox reactions in the system. As an example, if the redox species exists in bulk solution in oxidation state Ox, the sample can be polarized to electrochemically convert species Ox to species Red. If the tip is polarized to a different level, it is sufficient to cause an electrochemical reaction with Red. Initially no bulk current is generated at the tip, as the initial concentration of Red is negligible. However, when the tip enters a space where the products of the electrochemical reaction at the sample (Red) do exist, current will be generated at the probe. This provides an imaging mechanism for the probe to determine spatially where on the surface of the sample is most efficiently undergoing the electrochemical reactions. A high current at the tip is due to more concentration of Red at the probe, which is in turn due to a more active Ox→Red transition in that position.

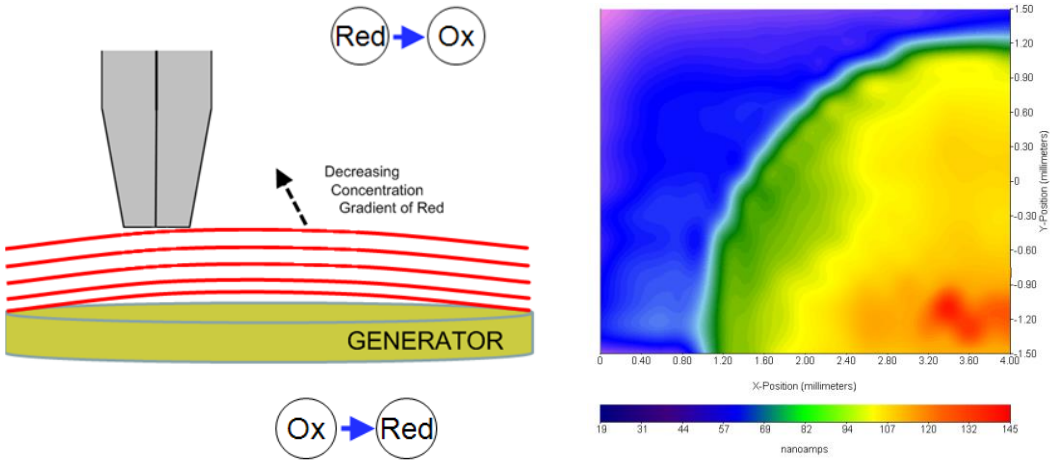


Figure 9. Example of Generator-Collector Mode

2.2 Applications

Since the imaging mechanism is electrochemistry, the applications of a SECM are as varied as the applications of electrochemistry itself. Some key applications are biological sensors, reaction kinetics, porous membrane study, fuel cell catalysts, and corrosion mechanisms.

2.3 VSC-SECM Packing List

Table 3. VSC-SECM Packing List

Description	Ametek PN	Quantity (Each)
Potentiostats		
VersaSTAT 4A*	VERSASTAT 4A-400VS	1
VersaSTAT 4A*	VERSASTAT 4A-400VSD	1
VersaSTAT 4A Cell Cable	224065	2
Spacer and Mounting Hardware*		
VersaSCAN Spacer	224134	1
Screw M3x0.5-20mm SHCS	233788	2
Washer M3 Flat, 7mm OD	233789	4
Screw M3x0.5-14mm SHCS	233792	2
Probe Mounting Hardware		
VersaSCAN Probe Mount	224063	1
VersaSCAN Probe Holder	224062	1
Screw 8-32x1/8”LG, Slotted Nylon	233790	2
Nut, Thin Hex, M10x1.5, 5mm HT	233866	1
Probes		
VersaSCAN SECM Probe, 10µm	224098	1
VersaSCAN SECM Probe, 25µm	224137	1
Test Sample		
VersaSCAN Gold Disk Test Sample*	224115	1
Clip, Alligator, Fang, Barrel, Steel	233868	2
Connectivity		
Extension Cord	803937	2
Cable, Trigger, SMA-BNC, 1m	1116486	1

*Indicates that item is used on multiple techniques and will not be duplicated in shipment.

2.4 Cable Connections for VSC-SECM

NOTE If the system has TWO motion controller boxes, please refer to Appendix 1 for set-up diagrams.

The diagrams are additionally available as part of the “Setup” of each experiment.

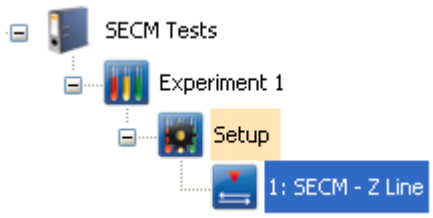


Figure 10. SECM Set-up Diagram

Cable Connections for a Potentiostatic controlled sample are below.

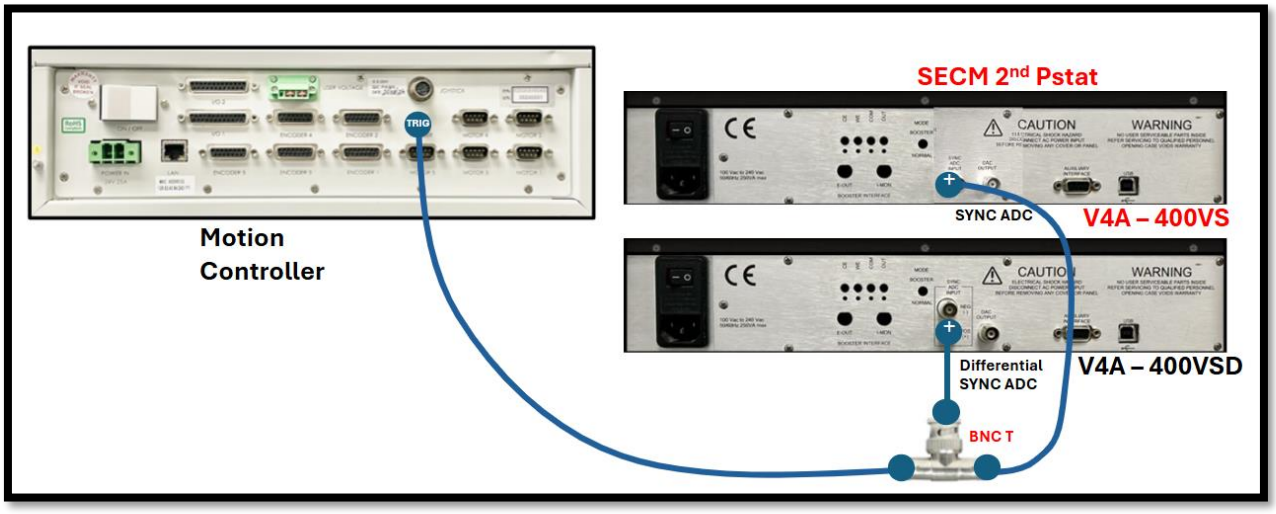


Figure 11. Connection Diagram for VSC-SECM

NOTE In Figure 11, the BNC T piece image is shown for reference only.

Table 4. Cell Connections for SECM

OUT	IN	CABLE
Diff. Sync ADC (+) of V4A-400VSD	T-BNC	BNC Cable
Sync ADC of V4A-400VS	T-BNC	BNC Cable
T-BNC	'Trig' on Motion Controller	BNC-to-SMA

NOTE In an Approach Curve experiment operating in Feedback Mode only one potentiostat is required. Connect the motion controller TRIG port directly to the potentiostat SYNC ADC using the BNC cable provided.

The VersaSTATs are connected to the electrochemical cell using the cell cable. As the only difference between the VersaSTAT 4A-400VSD and 4A-400VS is the differential Sync ADC, they have the same capabilities and accuracy. Therefore, any of them can be used to connect to the probe. The suggested configuration is to connect the VersaSTAT 4A-400VSD (w/ diff. Sync ADC) to the probe and the VersaSTAT 4A-400VS to the sample.

When two potentiostats are used for a single experiment, such as the Generator-Collector experiment, at least one potentiostat must be floating ground (e.g., VersaSTAT 4A-400VSD). Here are some example configurations using two Potentiostats.

Example 1: Feedback Mode, Single Potentiostat

Table 5. Potentiostat Connections for VSC-SECM in Feedback Mode

Potentiostat Lead	Cell Connection
VersaSTAT 4A-400VSD Working (Green) VersaSTAT 4A-400VSD Sense (Gray)	Probe, Tip
VersaSTAT 4A-400VSD Reference (White)	Common Reference Electrode
VersaSTAT 4A-400VSD Counter (Red)	Common Counter Electrode

Example 2: Generator-Collector Mode, 2 Potentiostats

Table 6. Potentiostat Connections for VSC-SECM in Generator-Collector Mode

Potentiostat Lead	Cell Connection
VersaSTAT 4A-400VSD Working (Green) VersaSTAT 4A-400VSD Sense (Gray)	Probe, Tip
VersaSTAT 4A-400VSD Reference (White) VersaSTAT 4A-400VS Reference (White)	Common Reference Electrode
VersaSTAT 4A-400VSD Counter (Red) VersaSTAT 4A-400VS Counter (Red)	Common Counter Electrode
VersaSTAT 4A-400VS Working (Green) VersaSTAT 4A-400VS Sense (Gray)	Test Sample

When multiple potentiostats are connected to the system, the VersaSCAN software must be told which one is connected to the probe, and which one is connected to the sample. Once both the potentiostats are located in the System Tab, the Hardware Requirements Tab is accessed by highlighting “Setup” in the Project Tab.

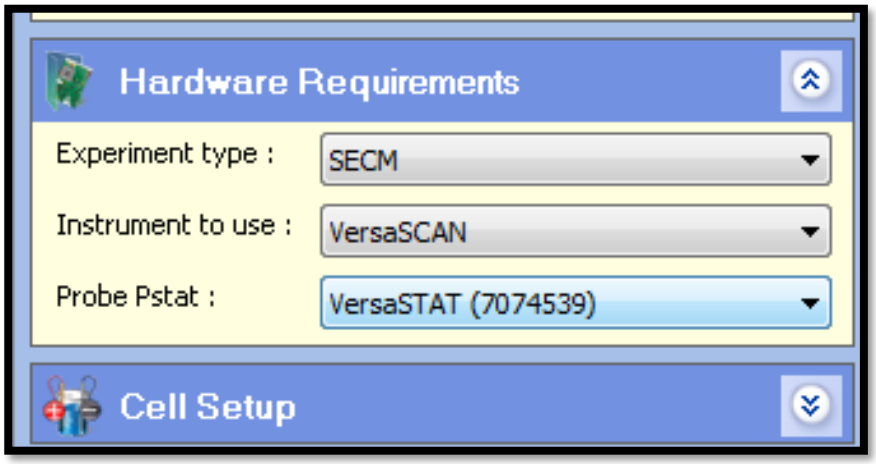


Figure 12. Hardware Requirements Screen

NOTE In Figure 12, it is necessary to specify the probe potentiostat and experiment type.

2.5 Software Control for VSC-SECM

2.5.1 Comments

Any comments that need to be stored with the data file can be entered into this field.

Please note that all the Scan and Measurement parameters from the experiments are already stored in each data file, so those are not necessary to be entered here.

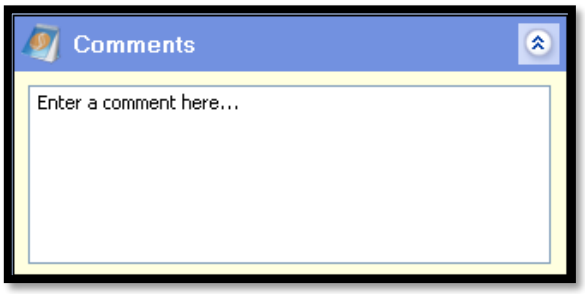


Figure 13. Comments Field

2.5.2 Conditioning

The conditioning tab allows the user to set the time for the system to be delayed before any measurement in the Step is started. Note this programmed delay occurs once before the experiment starts. The Measurement and Delay window allows other specific delays between each line and between each point to be programmed. The units for the description of time are also selectable.



Figure 14. Conditioning

2.5.3 Scan Setup

Scan Setup is a generic tab that has a familiar look and feel in all the techniques.

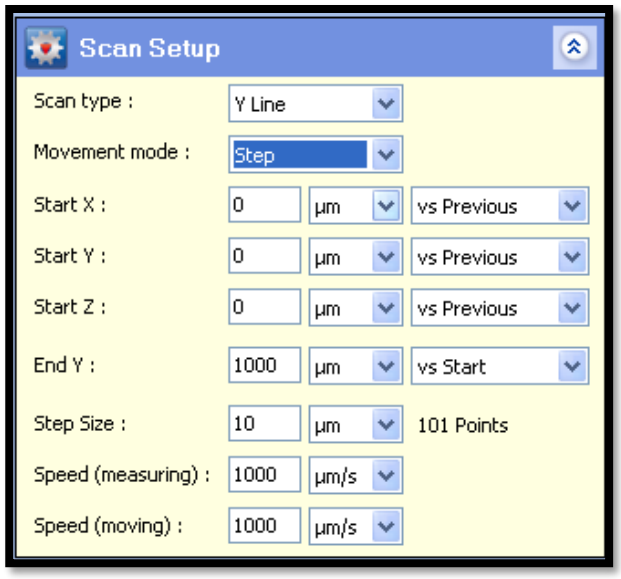


Figure 15. Scan Setup Screen

2.5.4 Scan Type

The “Scan type” allows the user to define if the experiment is going to be executed in a single line axis or in an area as a series of line experiments. “X Line” would be a single line of data in X, while maintaining a constant Y and Z position. “Y-Line” scans in Y as “Z Line” scans in Z.

“XY Area” will map an Area in the XY plane. This is accomplished by a series of X scans at different Y positions. Data acquisition occurs as the probe moves from Start X to End X (e.g., for -X to +X this is left to right).

“Point” will execute the experiment without moving the probe.

2.5.5 Measurement Mode

In a Z-Line experiment, such as used for an Approach Curve experiment, VersaSCAN acquires data in STEP Mode to decrease the opportunity for a tip crash.

In “STEP” will oversample and average the data. The probe moves to a given location and remains in that location for the measurement duration. Then, it moves stepwise to the new location (1 x Step Size: here 10 microns). Oversampled data collection again occurs at the new location; data is averaged and reported. This oversampling and averaging process reduces the noise in the experiment but increases the duration of the experiment.

“SWEEP” will acquire data while the probe is moving. Data is not oversampled, which decreases the overall duration of the experiment, but may affect data quality. Time Constant of the signal chain should be considered when setting the Sweep parameters, as the probe’s position is changing as data is coming from the signal chain.

2.5.6 Start X / Y / Z

In this field, the user defines the specific position that the experiment starts.

This can be set as "vs. Previous" or "vs. Absolute".

"vs. Previous" will allow the probe to use its current position as the origin point. In this example, 0 / 0 / 0 vs. Previous starts the experiment from the probe's current position.

"vs. Absolute" will use the known extreme position in order to keep an absolute reference grid from which positions are specified. 0 / 0 /0 would be the far left (-X) ; back (-Y) and down (-Z).

2.5.7 End vs. Start

In this field, the user defines the location where the experiment is terminated.

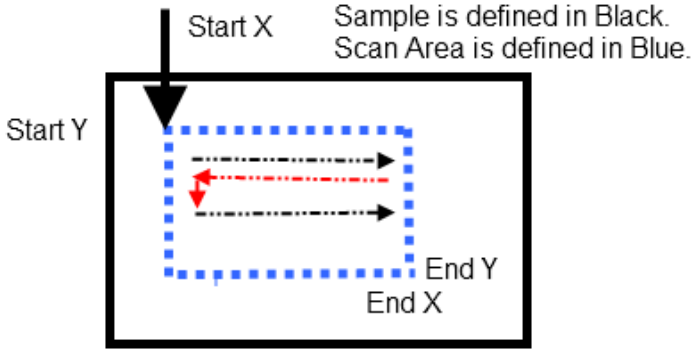
The "Start" and "End" define the distance or area over which the experiment is performed.

The dimensions of the Scan Area should be considered when Aspect Ratio of the data of the end-result.

2.5.8 Step Size

This field defines the data point density. A data point is acquired and recorded at every Step size. High resolution experiments would require small step size as one component.

In Area Scan, the user can define different densities in X and Y. Pixels do not have to be squares (equal X and Y) but it is recommended and set as the default.



Data acquisition happens along the Black dotted lines
At speed measuring taking data at every step size
Probe returns in the red line direction at Speed Moving

Figure 16. Area Scan Example

2.5.9 Measurement Mode Setup

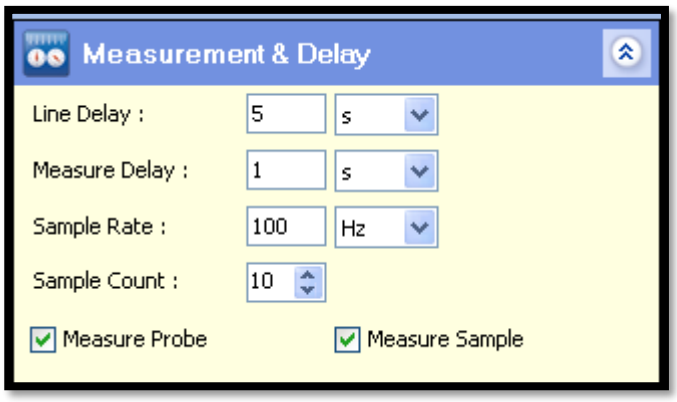


Figure 17. Measurement Mode Setup

2.5.10 Line Delay

The Line Delay allows the user to program a set time delay between each line of data acquisition.

This is helpful when waiting for motion in the electrolyte (convection) caused by the return scan to settle. Additionally, highly filtered data (long Time Constants) can benefit from using this to allow the data to exit the filter.

2.5.11 Measure Delay

This mode is available in STEP mode only.

This complementary delay is at every point during the scan.

Conditioning: Delay at the start of the experiment.

Line Delay: Delay is at the start of each line.

Measure Delay: Delay is at each data point.

2.5.12 Measure Probe and Measure Sample

This parameter allows the user to select or deselect to activate the measurement of either the probe or sample or both.

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3. VSC-SECM SYSTEM TEST PROCEDURE FOR GOLD DISK TEST SAMPLE

3.1 Materials

Please have the following prepared:
Potassium Ferricyanide (Hexacyanoferrate(III))/Potassium Chloride solution with the following molar content:

Potassium Ferricyanide (Hexacyanoferrate(III)) $K_3Fe(CN)_6$ – 5mM.

CAS Number 13746-66-2

Potassium Chloride – KCl – 100mM

If users are using the VersaSCAN mLCELL they will need a small volume of approximately 15 mL of solution. If users are using the larger VersaSCAN LCELL, they will need nearly 1000 mL (1L) of solution.

1200 Grit polishing paper or finer (1500/1800/2400 etc.), one piece

Napped polishing cloth, one piece

Alumina-oxide polishing suspension with particle size around 1micron

De-ionized water

3.2 Setup

1. Place the small air-bubble leveling device (P/N 233865) on the base (P/N 233752) of the SECM, in the position where the VersaSCAN mLCELL will be located. Level the base of the SECM using the 4 vibration resistant feet (P/N 233916) supplied.

2. Place a small amount of alumina-oxide (Al_2O_3) suspension onto the napped polishing cloth, then add de-ionized water to wet the cloth. Take the 5mm gold test sample (P/N 224115) and polish it on the cloth containing Al_2O_3 and water. Move in a figure-of-8 motion for a few minutes to ensure the gold/insulator is clean. Rinse thoroughly with de-ionized water to remove any Al_2O_3 suspension.

3. Place the sample into the VersaSCAN mLCELL and ensure it is a good fit so that it is watertight. If loose, add some PTFE tape to bulk-out the sample and make a fit. If tight, use some water or a small amount of grease placed on the O-ring to ease the sample into the VersaSCAN mLCELL. Mount the VersaSCAN mLCELL base onto the steel base of the SECM and orientate the three leveling screws in such a way that the window of the VersaSCAN mLCELL faces in the direction of the VSC-CAM (option). This can be done by adjusting the Allen-key screw that attaches the VersaSCAN mLCELL pillar to the thumb-screw plate. Next, attach the top of the VersaSCAN mLCELL to its bottom half by attaching

the cross-springs (O-rings, P/N 233754) between the two sections. Finally, place the bubble-leveling device onto the gold-test sample surface and ensure that it is level by adjusting the thumb screws.

4. Now fill the VersaSCAN mLCELL with the Test Solution, to around 70% of maximum. Insert the CE platinum (P/N K0266) and also the Reference electrode (P/N K0265) into the VersaSCAN mLCELL recesses in the PTFE body.

5. Take both Cell cables (each with CE, RE and WE) and attach both CEs of the cell leads to the CE. Attach both REs of the cell cables to the RE being used. The WEs will be treated in a moment.

6. Go to the PC application and select open an experiment (any will do, let's say CV for now). Go to the Experiment menu and see the following:

   VersaStudio may already be installed on the system. If not, users can download and install the latest version from www.ameteksi.com.



Figure 18. VersaStudio Icon

   There are two potentiostats with the SECM. At least one of the potentiostats must be floating ground. A standard supplied configuration is 2 x VersaSTAT 4A.

   It is suggested to start with a large diameter probe while getting familiar with testing mechanics and anticipated responses. Probe area is a factor that impacts response, so larger probes have better electrochemical sensitivity.

   As the only difference between the VersaSTAT 4A-400VSD and 4A-400VS is the differential Sync ADC, they have the same capabilities and accuracy. Therefore, any of them can be used to connect to the probe. The suggested configuration is to connect the VersaSTAT 4A-400VSD (w/ diff. Sync ADC) to the probe and the VersaSTAT 4A-400VS to the sample. Users will need to connect the Working + Sense leads.

   After all connections, there should be 2 x CE leads to the Counter Electrode, 2 x RE leads to the Reference Electrode, 1 x WE + 1 x Sense leads of the V4A-400VSD to the probe; 1 x WE + 1 x Sense leads of the V4A-400VS to the sample.

7. Lower the probe tip into the solution but keep it away from the sample at the current time.

8. Configure the CV as follows:

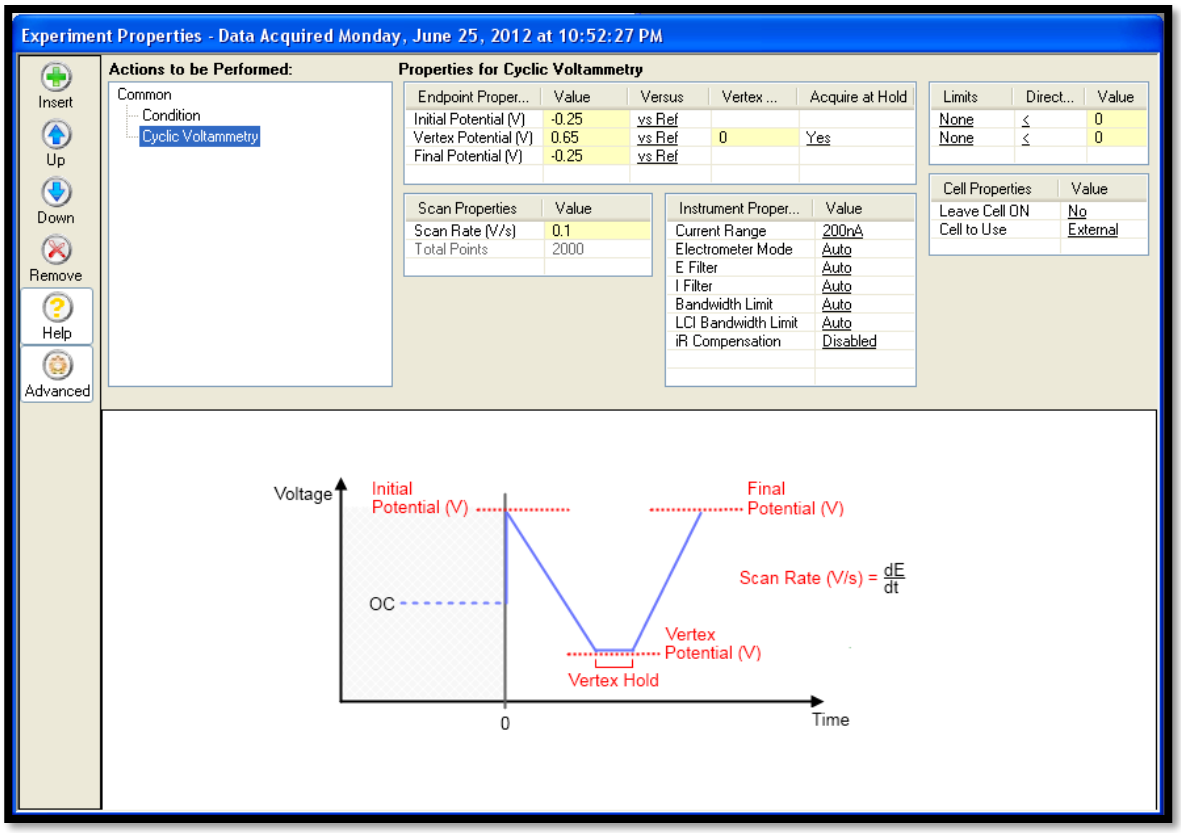


Figure 19. Experiment Properties

9. Run the experiment and the following is similar to what users should see:

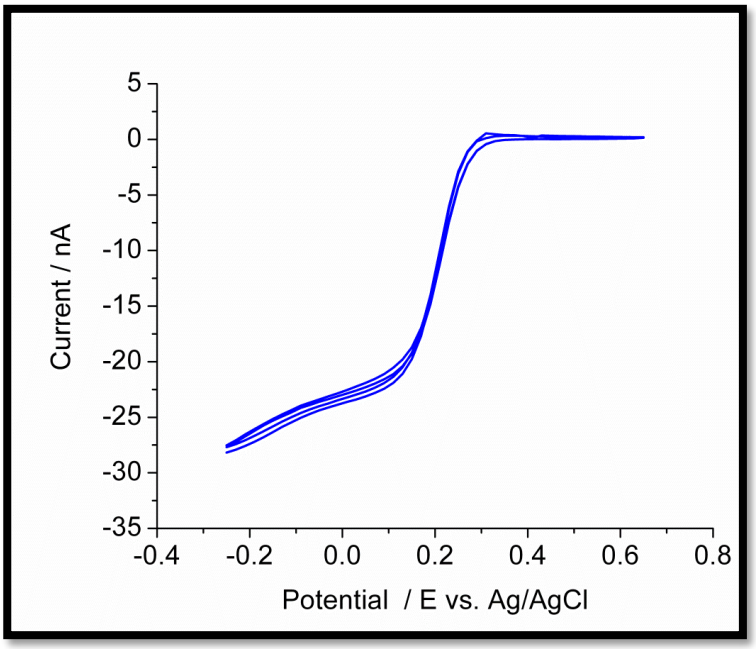


Figure 20. Experiment Results

The Sigmoid-shaped response is characteristic of an ultramicroelectrode. Note there is virtually no current flowing at the 0.65 Volts vs. Ag/AgCl, because iron exists in solution as the oxidized state Fe^{3+}. When the voltage of the Pt probe is swept to the reducing potential of -0.25 Volts vs. Ag/AgCl, Fe^{3+} undergoes an electrochemical reaction to Fe^{2+} and current flows.

Note, the level of currents expected for a 25-µm electrode.

If users see low currents or distorted or noisy traces, it is likely that the probe tip needs to be polished. This is a delicate job to do but must be done in order to achieve results similar to those seen above (in shape & approximate magnitude).

To polish the probe, apply a small amount of 1micron Al_2O_3 solution to the napped cloth and add de-ionized water to wet the solution further. Touch the tip of the probe to the cloth and perform a very small figure-of-8 motion. After a few tens of seconds, rinse the probe with de-ionized water and place the probe back in the SECM, connect the correct WE and re-run the CV experiment. Repeat this until the user is satisfied that the shape is somewhere close to the desired shape/magnitude.

10. Save the results of the CV.

11. Now go to the Tools → Select Instrument menu and select potentiostat that is connected to the gold sample.

12. Set the current range to 200µA range.

13. Now run the experiment and see the following CV at the end of the experiment –

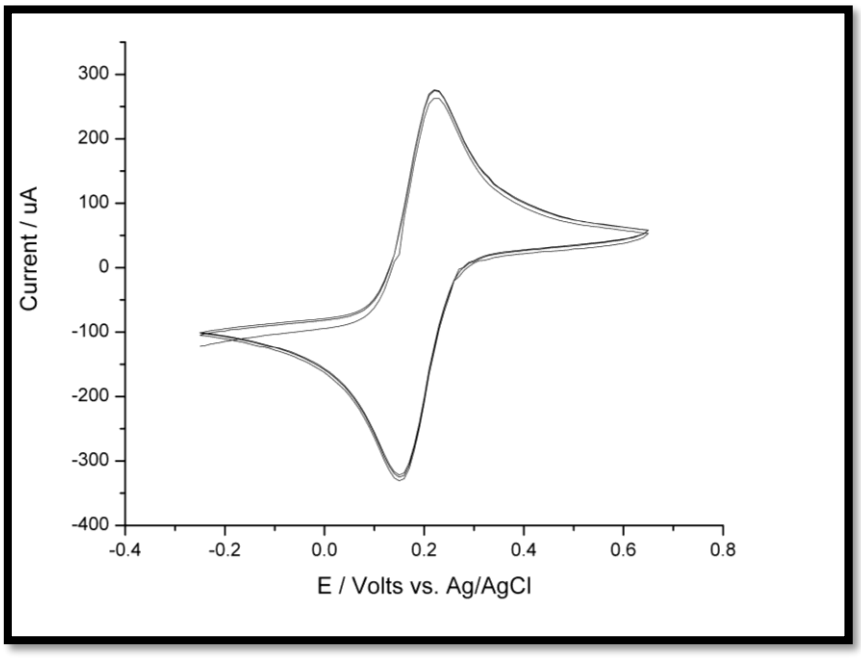


Figure 21. CV of 5mm Gold Sample

This is a CV of the 5mm gold sample. Notice the difference in shape to the 25-µm probe.

3.3 Running Approach Curves

Approach Curves define when a probe enters the local imaging area.

1. Select a Z-Line Scan SECM experiment to run an Approach-curve experiment. Move the tip over the Insulating part of the sample (not the gold, but the epoxy region) using the X/Y/Z parameters at the Manual Position window. If users are new to moving the probe in this fashion, remove the probe first and practice before replacing the probe.

2. Using the VSC-CAM or visually, bring the tip of the probe to some 'close-proximity' to the surface. 1mm distance is fine for the moment. Do not try to get the probe too close!!!

3. Configure the approach curve as follows:

   Apply -0.25 Volts to the Probe. This will cause the electrochemical reduction of Fe^{3+} at the probe and current will flow. This should be approximately the same current that -0.25 Volts produced during the CV experiment at the probe.

   Points to note –
   - the potential of -0.25V is chosen from the CV – it as at this potential that the current is maximum and is not on an oxidation/reduction peak.
   - Conditioning time allows the cell to stabilize somewhat.
   - The scan range is set to -500 microns (for example) in the Z direction – the probe is going down towards the sample.
   - IMPORTANT – the step size is 10microns. This is related to the probe size. With a 25µm probe, the effect users are looking for will occur over, perhaps, 50 to 80 microns. Therefore, set the step size to well below this so that the effect is not missed and the probe crashes. For example, if a 10micron probe is being used, set the step size to 2 to 4 microns – no larger!

   STOP the probe movement with "Stop All" function on the tool bar when the local response in the Current versus Position graph is just becoming visible.

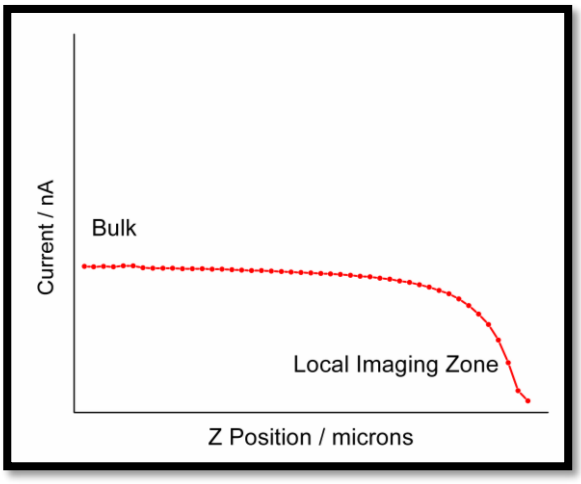


Figure 22. Current Versus Position for Insulator

4. Be aware that the probe will be approaching the surface at 10microns every second. It is the users' responsibility to watch for the decay of current and stop the experiment when the current starts to drop. If this is not done, the probe will crash and may break.

5. If the current does start to drop, and gets to 75% of its initial current, stop the experiment. Repeat this a few times and become more confident in the way that it works. Eventually, users will have a graph similar to the one shown in the supplied Sample Data file project.

6. Now reposition the probe over the gold and repeat all of the above for the conductor (please also read the next few points and text to make sure users understand what is expected and what happens). If by chance, a similar curve to the one shown for the insulator is seen, it is most likely because the sample is dirty and needs to be removed and re-polished, either mechanically or by electrochemically sweeping from -1 V to + 1 V at a fast rate e.g., 500 mV/sec for a few cycles, 10 cycles.

7. If the above process is repeated for the conductor, expect to see the following:

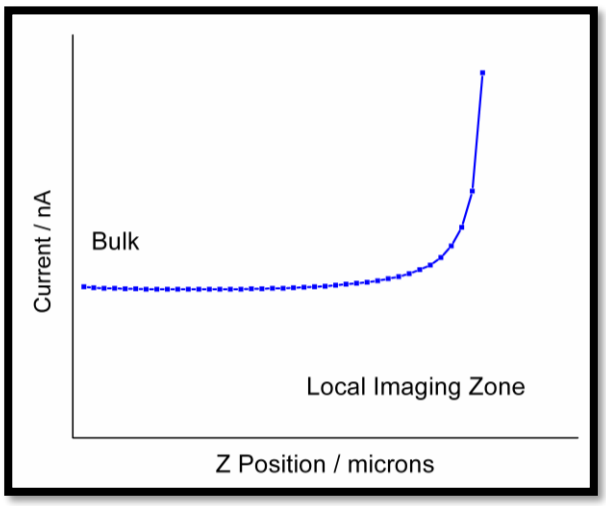


Figure 23. Current Versus Position for Conductor

Then, if these 2 plots are considered together, users can find a maximum difference.

Notice that the current starts around the same value of 40nA – the current seen when the probe is in the bulk of the solution (not near a surface). Also, what may not be very apparent here is that the upward trend of the conductors' response is faster than the downward trend of the insulator. This is why an approach to an insulator is performed first, simply because it is easier to do. Please note, the result above was taken with a 25µm probe.

8. If the sample is level/flat with respect to the probe scan in the X/Y axis, and users have moved the probe only a few millimeters to change from an insulating to conducting sample, then the two approach curves should coincide.

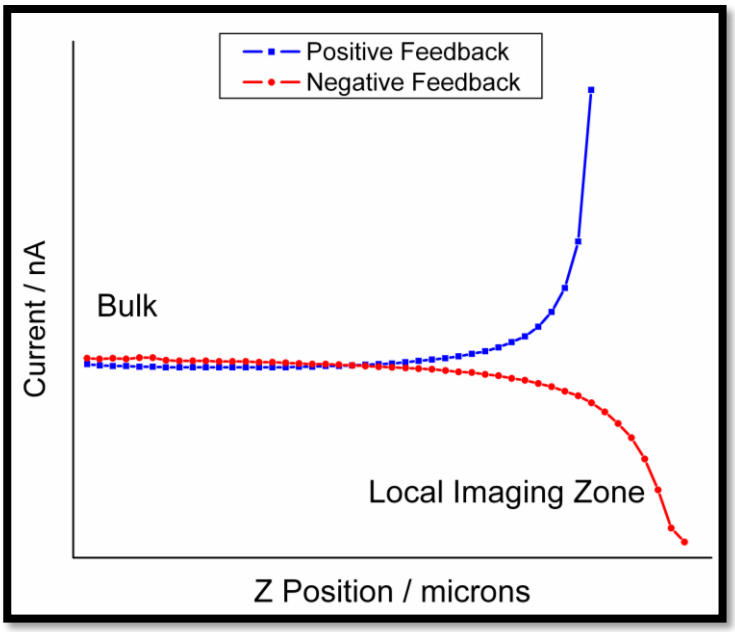


Figure 24. Insulator Versus Conductor Comparison

9. Now choose a Z-axis point, so that both inhibited and enhanced currents can be seen when over insulating and conducting regions respectively.

3.4 Line Scans and Area Maps

1. Place the probe tip at the chosen point in z, within 1mm of the edge of the sample.

IMPORTANT	Note that at the end of the experiment the probe stays at the ending location. Use a “Move” Step to return it to the original position. Now perform a line-scan experiment in such a way that the probe scans across the barrier (change in material).

2. Configure the experiment something like the example provided in the Sample Data project.

   The result that should be achieved, providing all has gone according to plan, is the following:

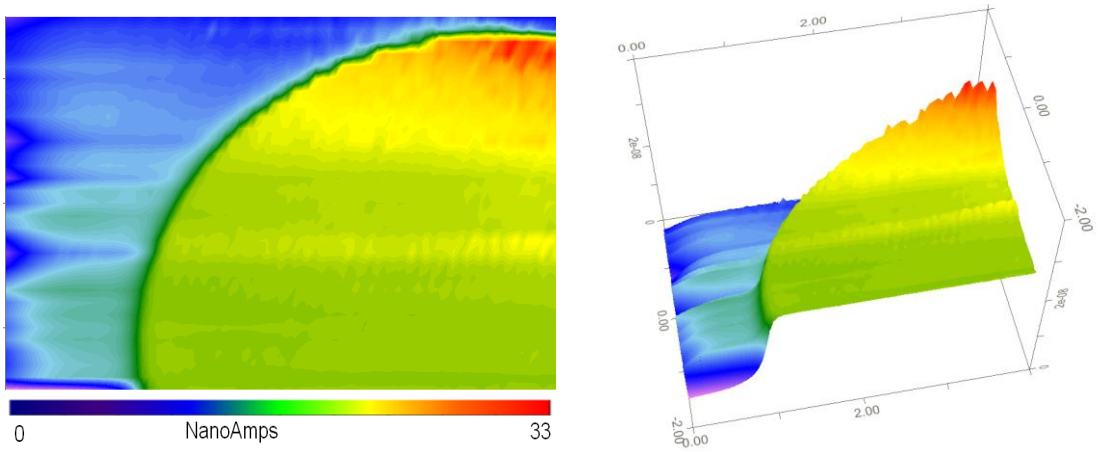


Figure 25. Area Maps

Notice the current is inhibited over the insulator (i.e., less than 40nA) and enhanced over the gold (i.e., more than 40nA). Please note, the result above was taken with a 25µm probe. If desired, users can configure an area scan experiment, using their own set-up values.

4. AC-SECM

4.1 Introduction

AC-SECM is a technique based upon impedance. In this experiment, the sample is usually not connected to the potentiostat. The key advantage of this technique versus traditional SECM is there is no requirement for an additional mediator. Therefore, the technique has great appeal to corrosion scientists since a mediator could affect the corrosion properties of the sample during scans.

The probe is connected to potentiostat with FRA enabled such as the V4A.

The theory of operation is very similar to traditional EIS measurements in which the probe tip potential is modulated using a small amplitude, fixed frequency signal. The impedance of the probe depends upon the electrochemical activity of the solution phase directly beneath the probe.

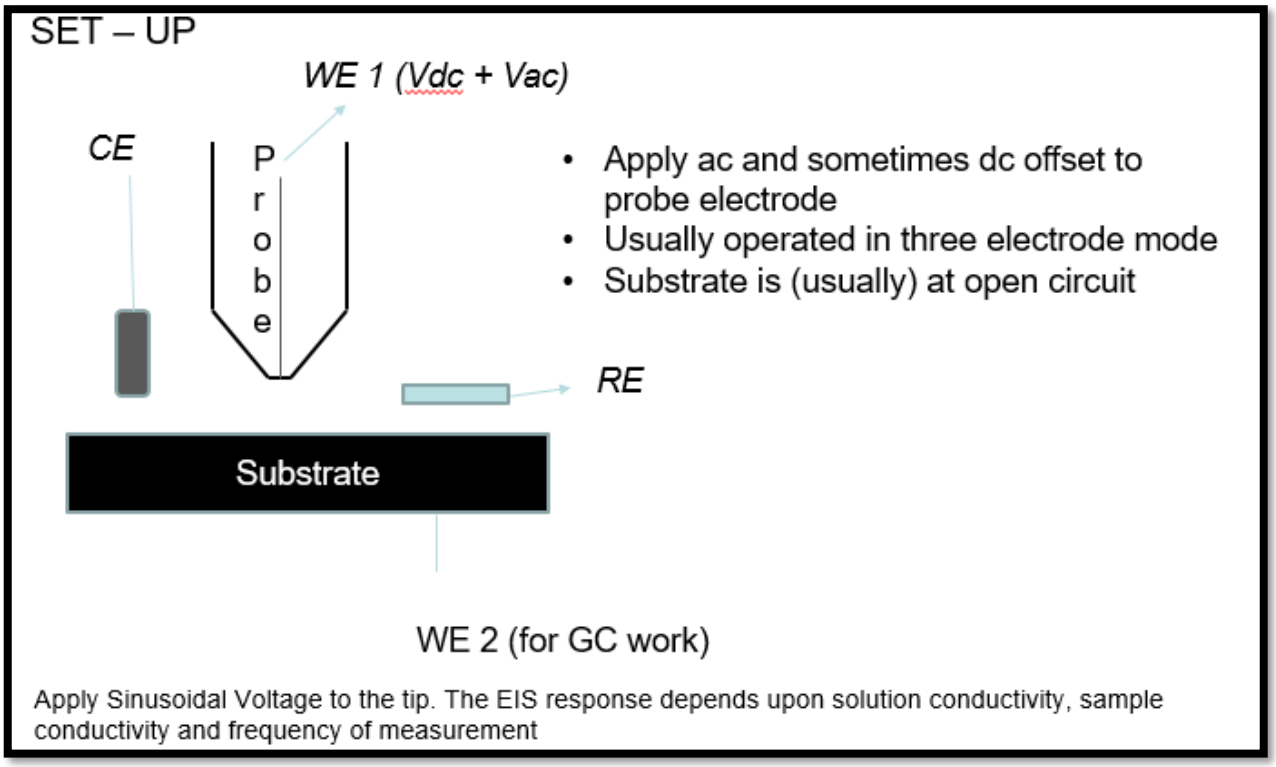


Figure 26. AC-SECM Setup

When the probe approaches the surface (within a couple of probe diameters), a feedback mechanism similar to that observed with traditional SECM is observed e.g., the impedance decreases when the tip approaches a conductor and increases when approaching an insulator.

However, AC-SECM results can be influenced by the frequency of the probe oscillation and the conductivity of the solution. This can result in an increase in the impedance of the probe measurement as the probe approaches both an insulator and a conductor. There are three limiting cases for AC-SECM measurements.

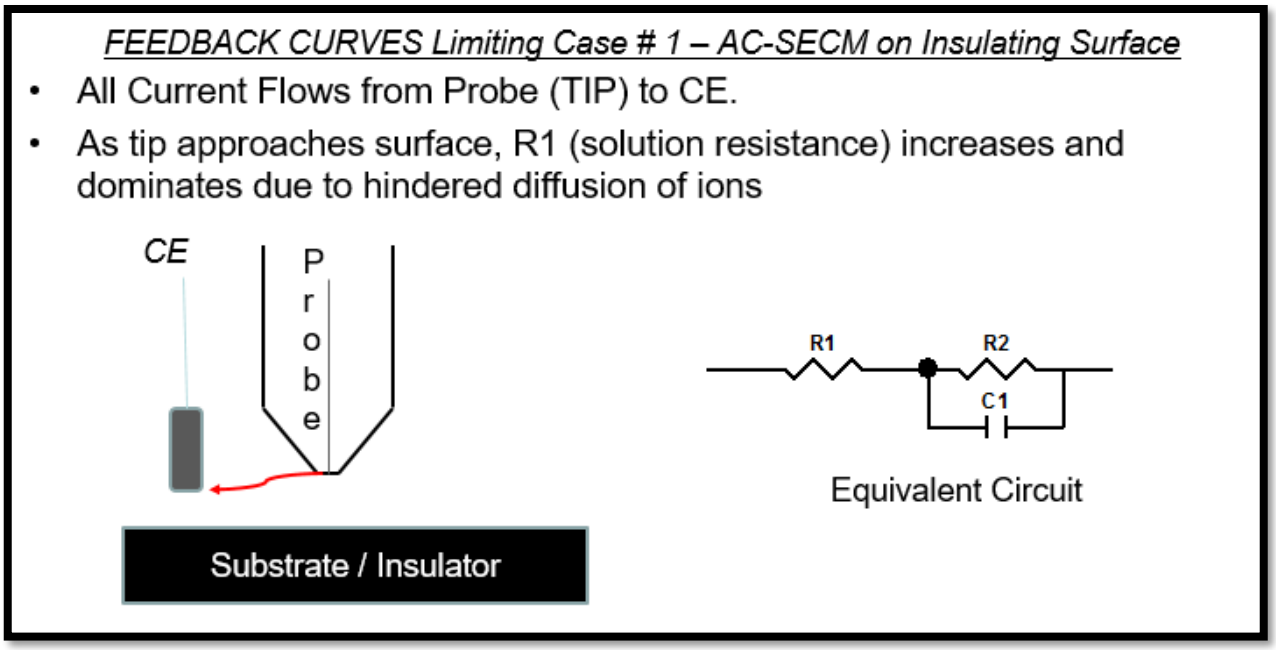


Figure 27. Limiting Case Number 1

Limiting Case #1: The current flow is shown by RED arrow. The approach curve for this substrate is similar to that of the DC SECM response in which hindered diffusion (migration) of ions results in an increased impedance.

Table 7. Limiting Case Number 1 Circuit Element Definitions

R1	Solution Resistance between Tip and Reference Electrode
R2	Faradaic Impedance of Tip
C1	Double Layer Capacitance of tip

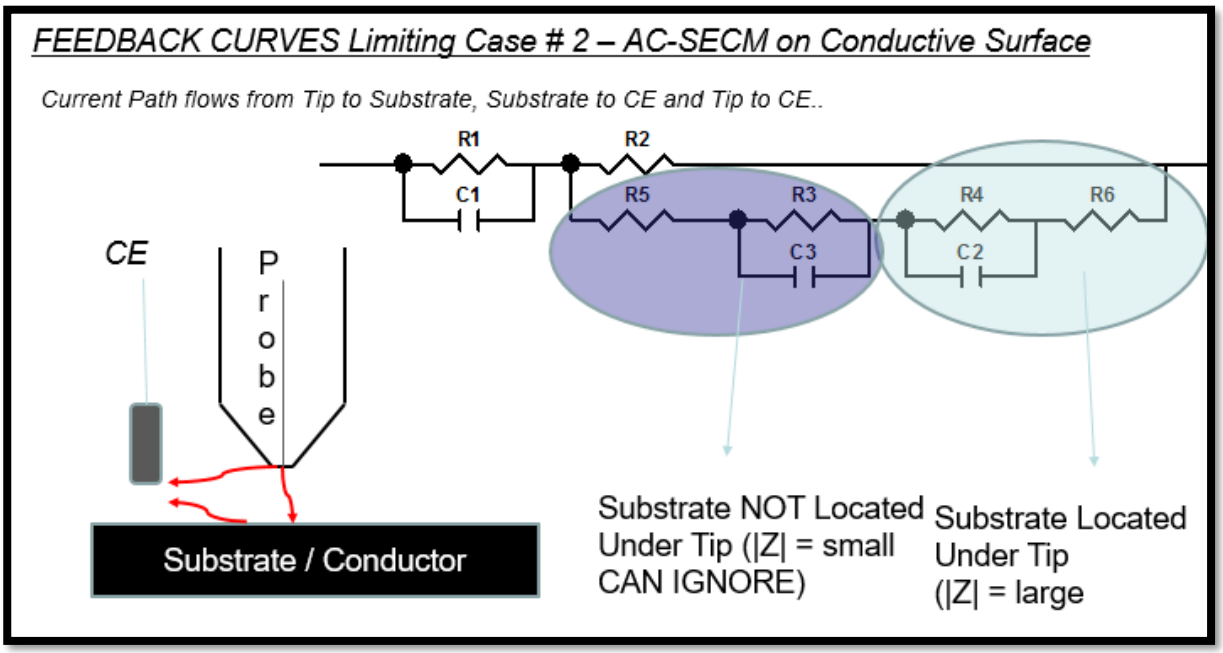


Figure 28. Limiting Case Number 2

Limiting Case #2: Current can now flow in multiple paths:

a) From probe to CE
b) From probe to CE via conductor

The equivalent circuit has been constructed to show this process – as shown in case #2.

Table 8. Limiting Case Number 2 Circuit Element Definitions

R1	Faradaic Impedance of Tip
R2	Solution Resistance between Tip and Reference Electrode
R3	Faradaic Impedance of Substrate NOT directly under Tip
R4	Faradaic Impedance of Substrate directly under Tip
R5	Solution Resistance between Reference Electrode and Substrate
R6	Solution Resistance between Tip and Substrate
C1	Double Layer Capacitance of tip
C2	Double Layer Capacitance of Substrate directly under Tip
C3	Double Layer Capacitance of Substrate NOT directly under Tip

Since the impedance between the between the part of the substrate NOT covered by the tip is small in comparison to the substrate directly under the tip, elements R3, R5, and C3 can be ignored.

The reduced equivalent circuit can now teach about the behavior of the systems as a function of electrolyte concentration and frequency.

A) High Frequency and/or Low Electrolyte Concentration.

In this case, the capacitances behave as a short circuit. Therefore, all current flows through elements R6, C2, and C1. This simplifies the impedance of the solution resistance between the tip and the substrate. As the distance decreases, the resistance (impedance) decreases. The current path is shown in RED arrows in the next figure.

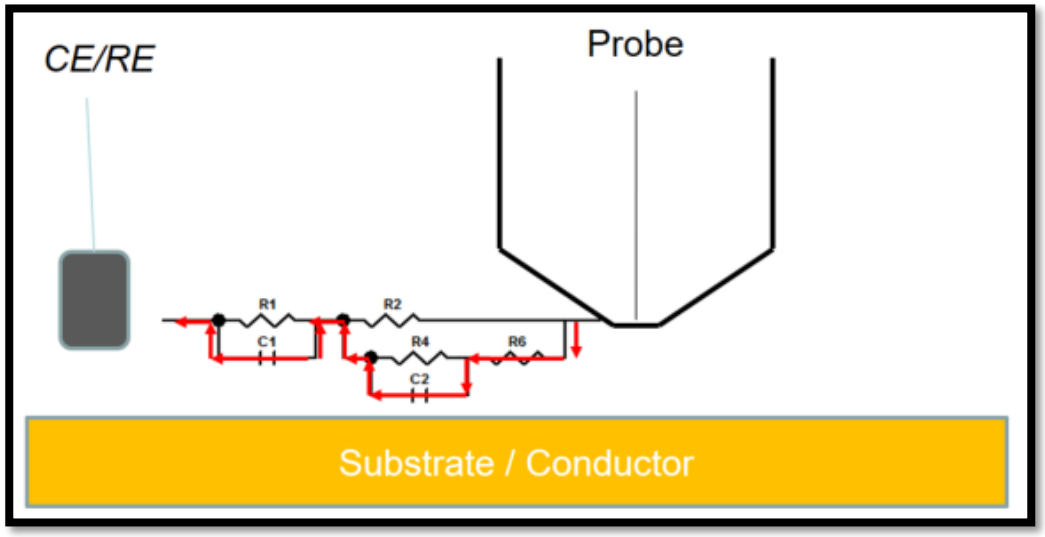


Figure 29. High Frequency and/or Low Electrolyte Concentration Current Flow

Current Flow (red arrows) for high frequency and/or low electrolyte concentration.

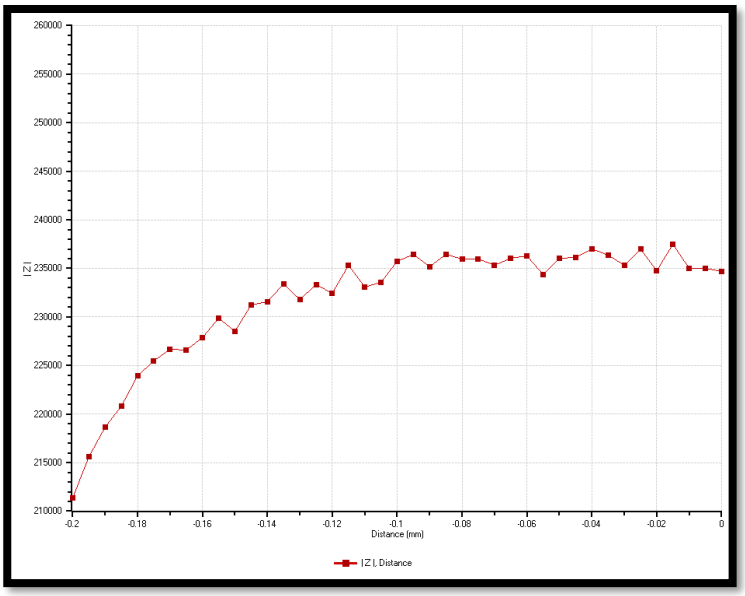


Figure 30. High Frequency and/or Low Electrolyte Concentration Graph

Typical Tip -Approach curve response for high frequency and/or low electrolyte concentration measurements over a conducting substrate.

B) Low Frequency and/or High Electrolyte Concentration

In this case, the current is limited by the solution resistance, R1 (current flow is shown in the figure below in the red arrow). Therefore, as the tip approached the surface, hindered diffusion of ions results in an approach curve resembling an insulator.

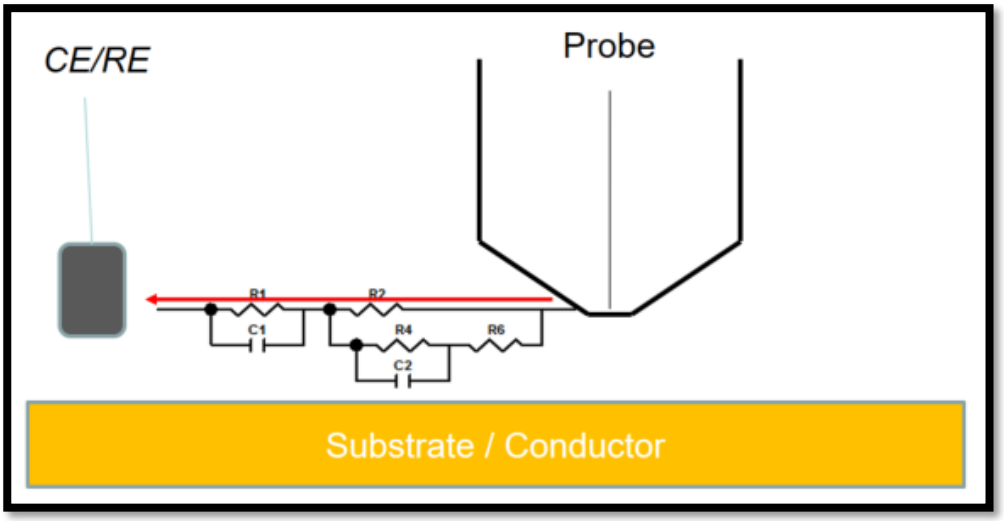


Figure 31. Low Frequency and/or High Electrolyte Concentration Current Flow

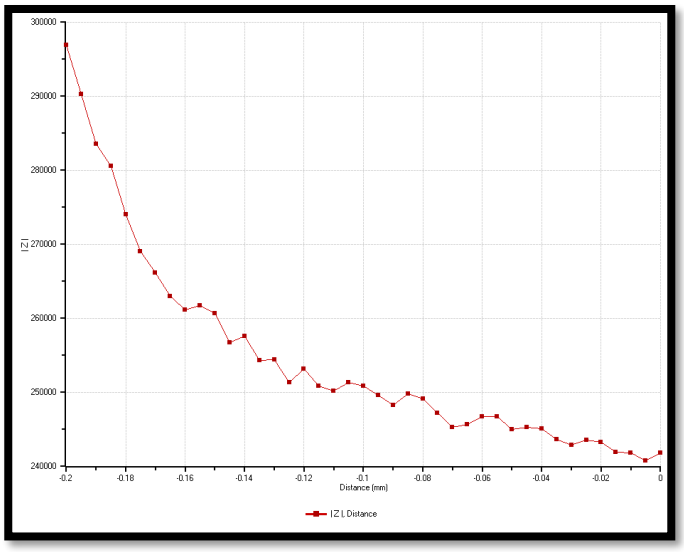


Figure 32. Low Frequency and/or High Electrolyte Concentration Graph

Typical Tip – Approach curve response for low frequency and/or high electrolyte concentration measurements over a conducting substrate.

4.2 Example Data

For this experiment users will need:

Gold Disk Sample, Reference Electrode, counter electrode, 10µm or 25µm Pt electrode. Users only need to use TAP WATER for this experiment. If the conductivity of the solution is too high, results can be difficult to interpret.

4.2.1 Approach Curves

1. Select Potentiostatic EIS technique in the operating mode. Polarize the Probe electrode to 0V vs Open circuit.

2. Chose Single Frequency Technique

3. Set the ac amplitude to 100mV (note – the system is highly linear and therefore large ac amplitudes can be used for this test)

4. Set the Frequency and integration period to 30kHz and 10 cycles respectively

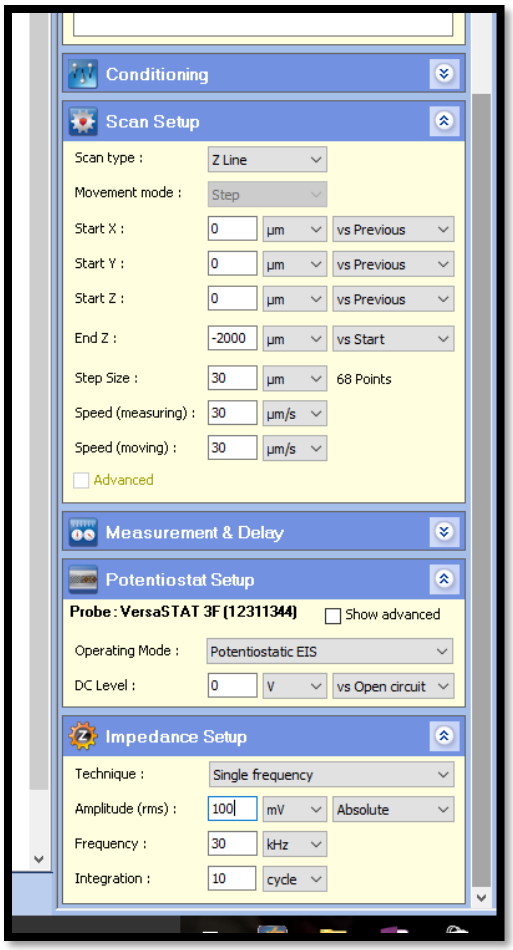


Figure 33. Scan Setup

5. Run the approach curve over the insulator and repeat over the conductor.
6. The Approach Curves for an insulator and conductor are show below.

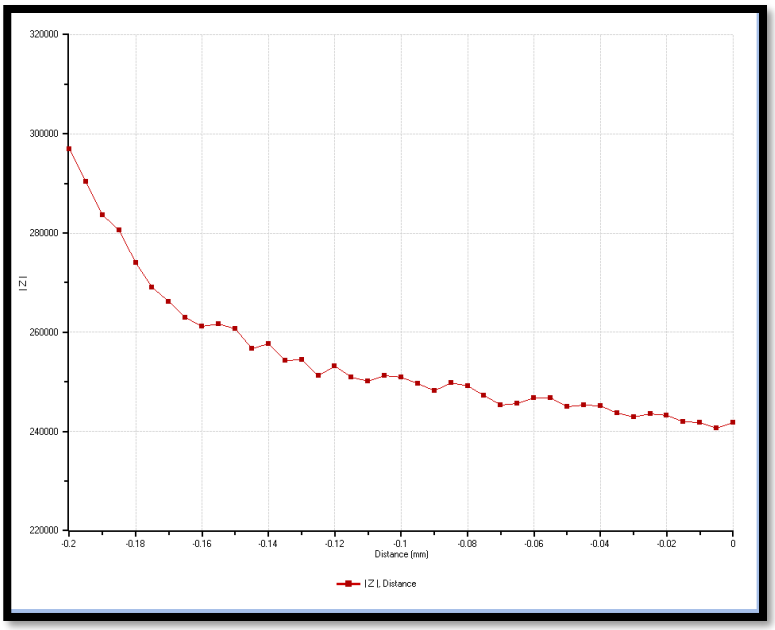


Figure 34. AC-SECM Approach Curve Response for an Insulator

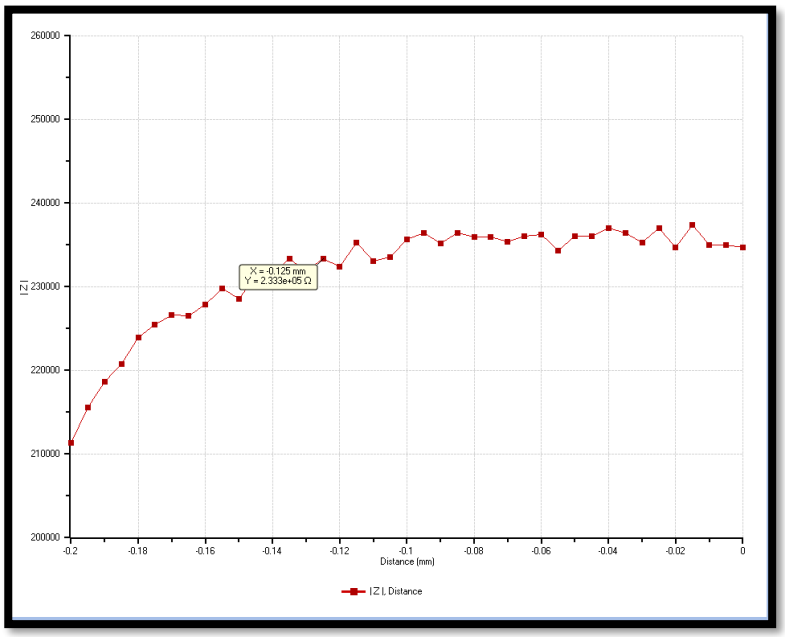


Figure 35. AC-SECM Approach Curve Response for a Conductor

NOTE The magnitude of the change can be quite small from bulk to surface.

4.2.2 Feedback Mode X-Y Scan

Position the probe in the local imaging zone as determined by comparing the approach curves over the insulator and conductor. Leave one of the VersaSTAT 4A disconnected and polarize the probe using the other VersaSTAT 4A at 0V vs OC. Run an X-Y scan in this Feedback mode configuration (the sample is not polarized).

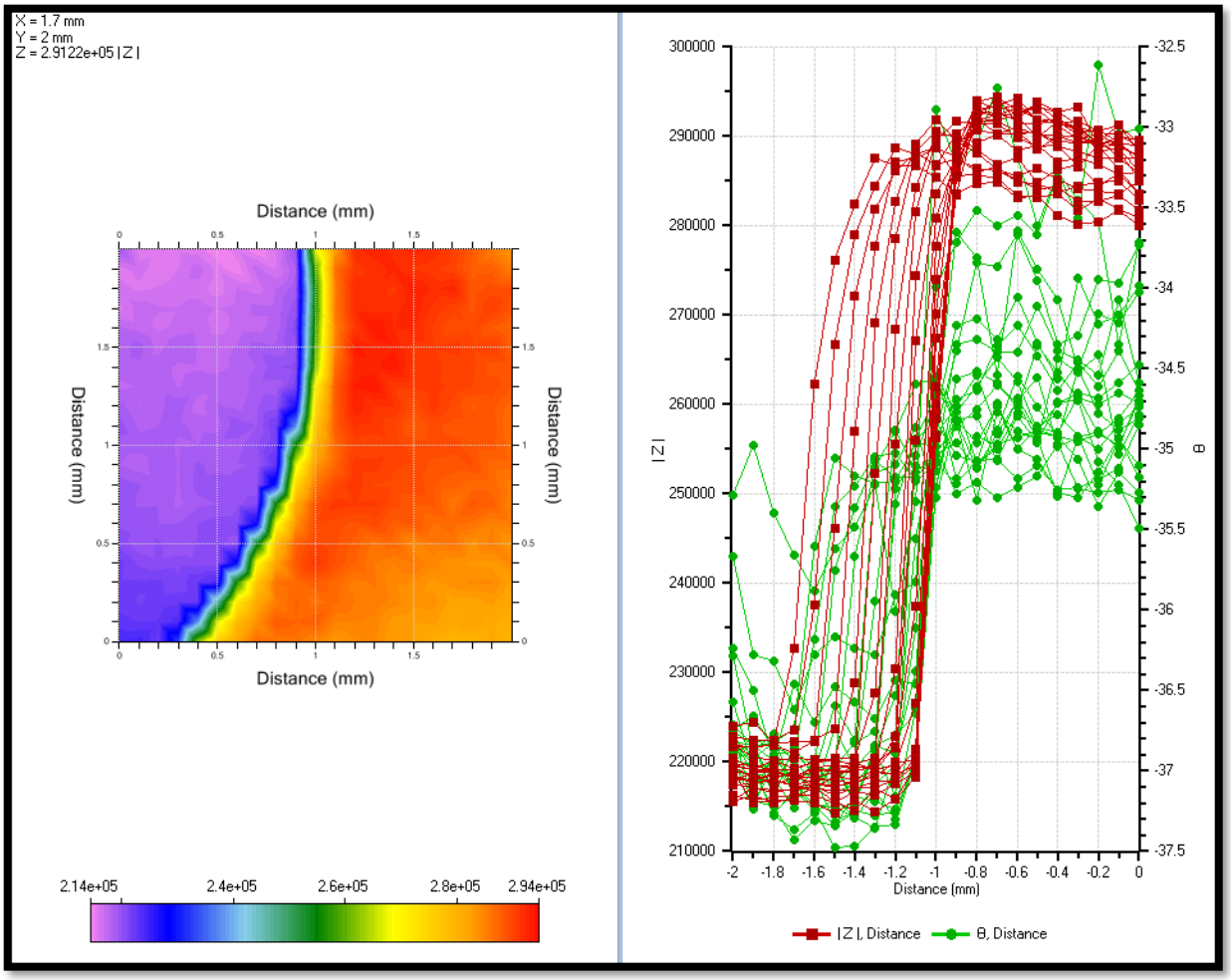


Figure 36. Typical Set of AC-SECM Results Across Insulator/Gold Sample

5. VSC-SOFT STYLUS PROBE SECM

This technique requires Soft Stylus Probe assembly (VSC-STYLUS).

5.1 Technique Overview and Introduction

The soft probes offer a simple and convenient method of maintaining a constant distance between the probe and the substrate. This is especially useful when trying to limit the effects of changes in surface topography for the electrochemical measurement signal.

The probe consists of a carbon electrode sealed in a flexible polymer sheath. A thin Insulation coating is applied to the film to provide the final sealing stage. The exposed diameter of the electrode is equivalent to approximately a 15µm dimeter electrode.

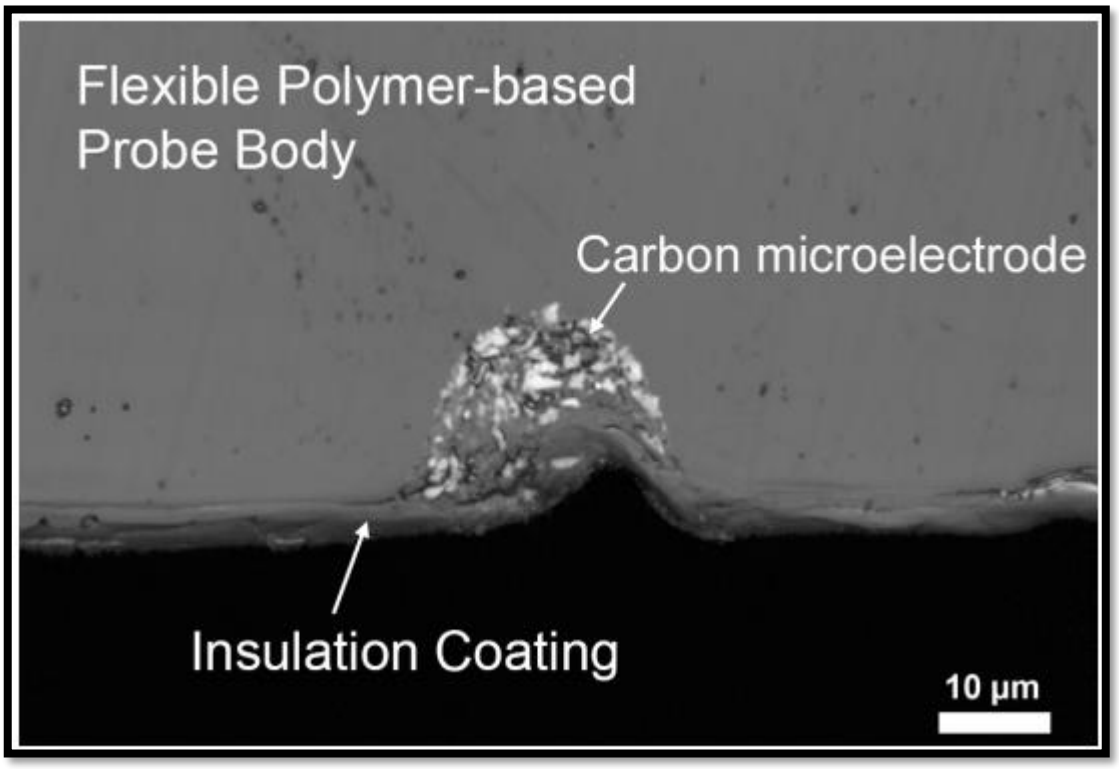


Figure 37. Cross Section of Carbon Probe After Cutting the Probe

5.2 Theory of Operation

It is instructive to understand how the probes work in 3 cases

i) in solution
ii) just touching the substrate
iii) in full contact regime as shown in the figure below

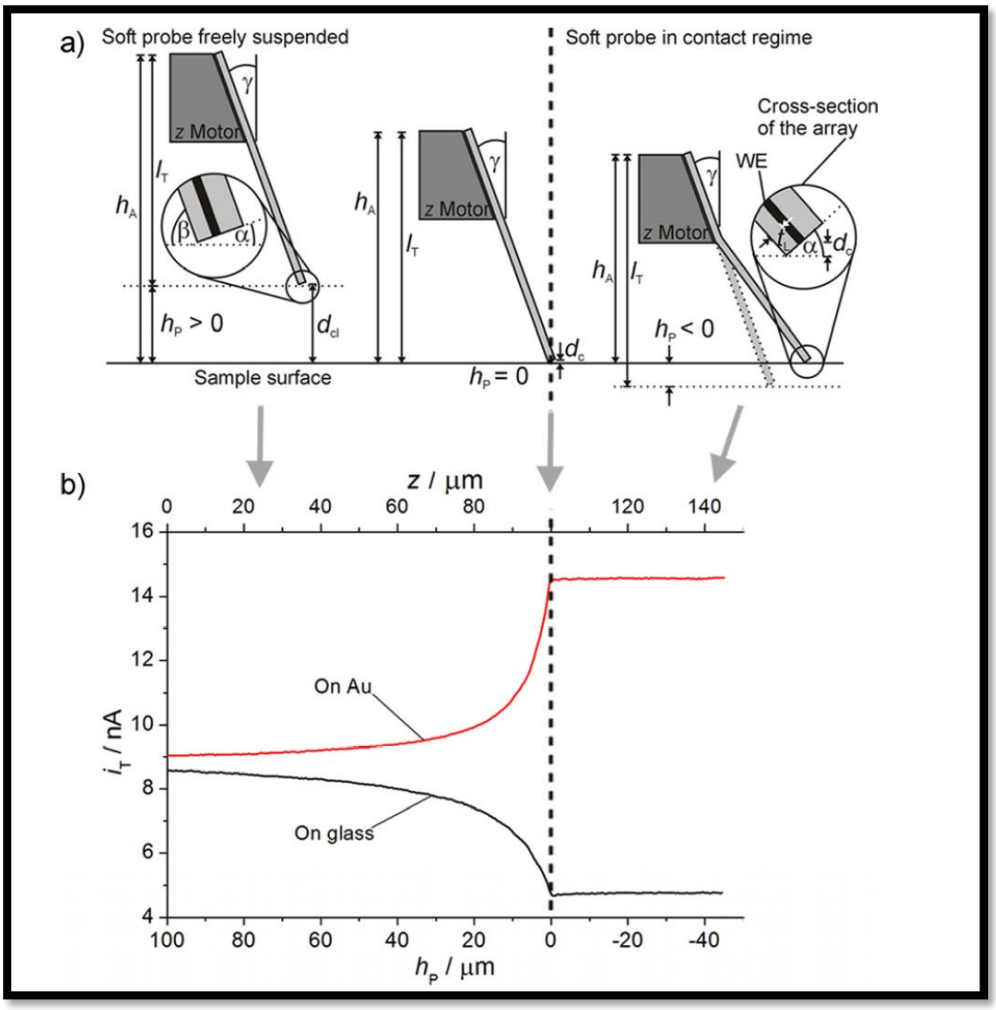


Figure 38. Examples of Probe Contact

- Figure A: The soft probe is freely suspended. The electrochemical signal is that of the bulk.
- Figure B: The soft probe is just in contact with the surface. Notice the classical approach curve response to an insulator and conductor respectively.

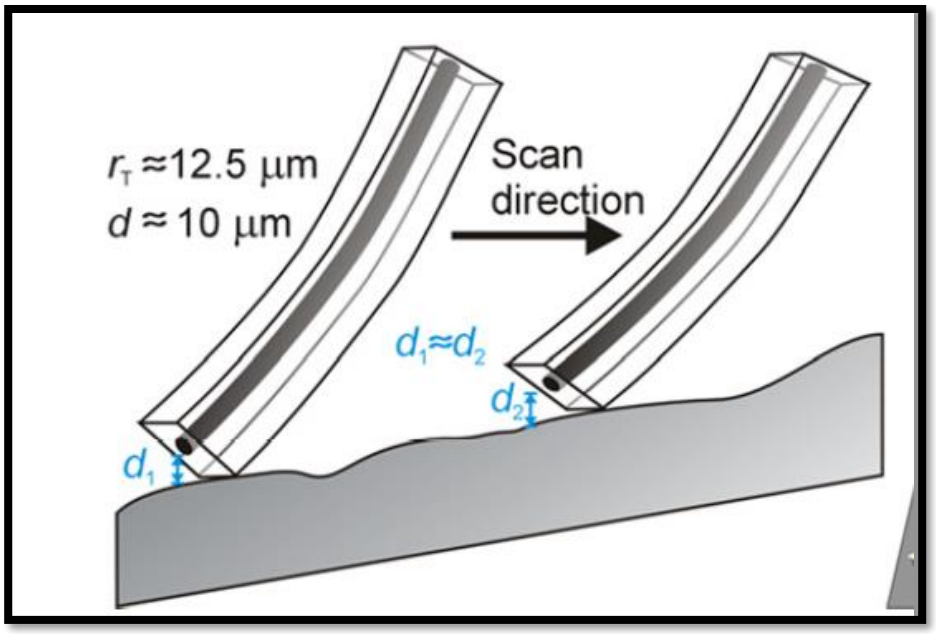


Figure 39. Probe Positioning

In the above image, the probe is 'pushed' into the surface. This is the correct mode for imaging. The current is independent of probe position in the Z direction for electrochemically homogeneous surfaces. Consequently, the technique provides a means to eliminate topographical effects from the electrochemical response.

The distance between the probe and the sample is controlled by a number of factors including the probe angle and the thickness of the Insulation coating (see image above). To achieve high contrast imaging, it might be necessary to adjust the probe angle close to perpendicular to the surface (this reduces the distance d_1 and d_2 in the image above). It is recommended that the user experiments with different probe angles to determine if this improves contrast imaging. An angle of 20 degrees is recommended to start experiments.

5.3 Probe Preparation and Handling

The following section describes how to set up the probe and insert the probe into the holder prior to measurements.

Probes are either delivered in a UNCUT or CUT configuration**.** The handling procedure for either of these configurations is the same.

The probes are coated with a thin insulation coating which can damage if handled incorrectly. Whilst the risk of damage is small, it is recommended to follow handling procedures.

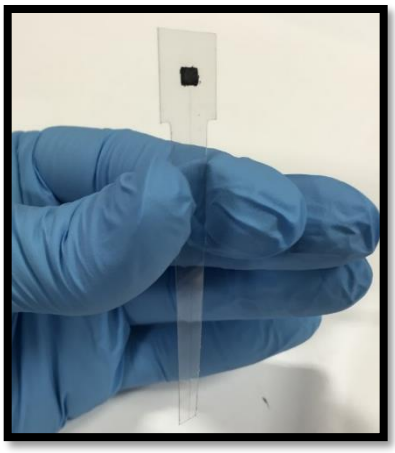


Figure 40. Probe Handing Example

Wear suitable gloves, to avoid smearing on the clear plastic probes. The gloves can be nitrile or vinyl (to avoid allergy issues associated with latex gloves).

- Avoid direct contact between the probe and the work surface as debris can scratch the Insulation coating. If it is needed to place the probe on a work surface during handling, place the probe on a cloth or clean sheet of paper to avoid direct contact with the work surface.
- It is preferable to handle the probes on the edges rather than on the faces. Whilst this is not always possible, minimizing handling the probes on the face will reduce the risk of accidental damage of the probe.
- The probes are designed to be highly flexible and therefore **no special precautions** should be taken to avoid bending the probes.

5.3.1 Probe Preparation

The probe needs to be cut using the scissors provided.

Alternatively, the probe can be trimmed with Razor blade (as shown in Figure 44), which is NOT supplied.

Cut the probe to the following dimensions. It is not critical to get this exact at this stage. The cut line is represented by the dashed line and the outline of the cut probe is represented as the darker shaded region.

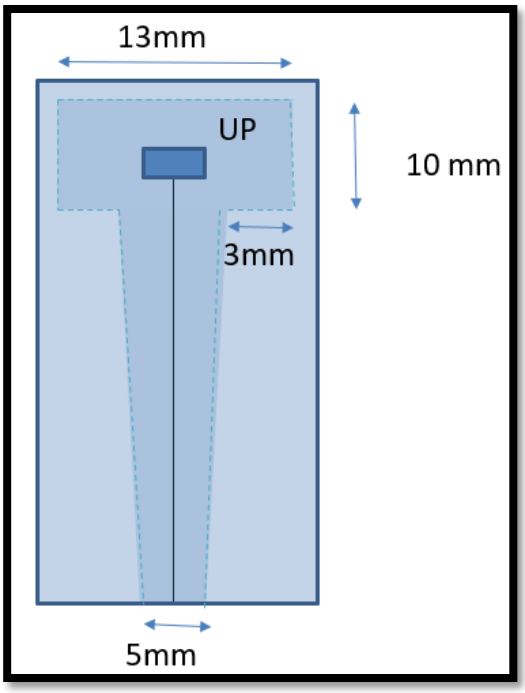


Figure 41. Probe Cutting Diagram

It is necessary to cut the probes to a fine taper using either the surgical scissors provided or a clean, new scalpel. The tapering of the probe will help the movement of the probe during operation. Whilst the width of the probe at the tip is not critical, in general, the smaller the width the better. It is suggested to use a width of approximately 1mm. The Figure 42 overleaf shows the cutting lines.

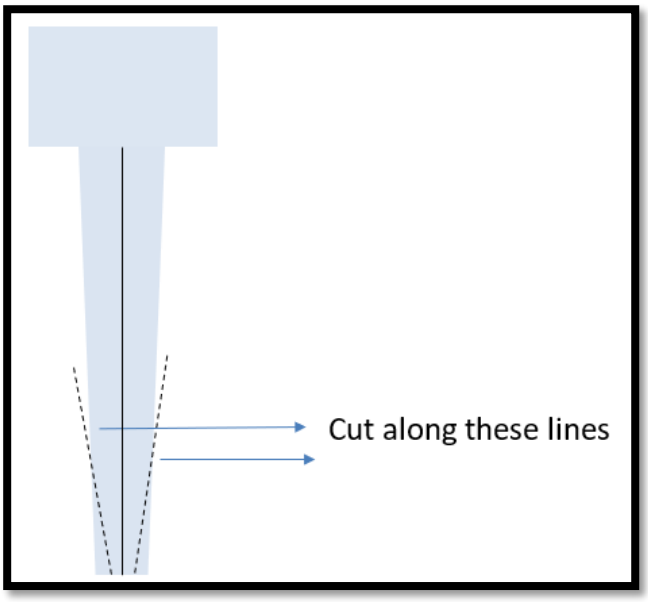


Figure 42. Probe Cutting Lines

The final probe is shown below. Note the fine tapering of the probe to a point.



Figure 43. Final Probe

The final stage requires preparation of the electrode surface. The razor tool will be needed for this final stage as it provides a clean cut.



Figure 44. Alternative Razor Tool for Probe Cutting

Place the probe on a smooth, flat surface.

Place the cutting tool at right angles to the probe tip as shown below. With practice, users can reduce the amount of probe cut. In this example, the new probe tip was cut about 0.5mm from the end of the probe. Be careful not to touch the cutting blade as it is extremely sharp.

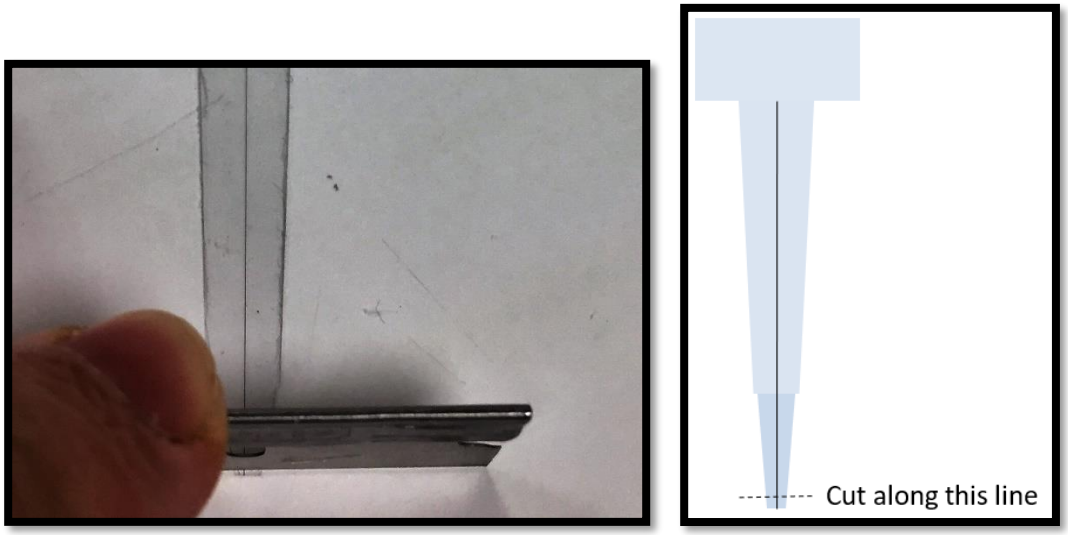


Figure 45. Probe Cutting Demonstration

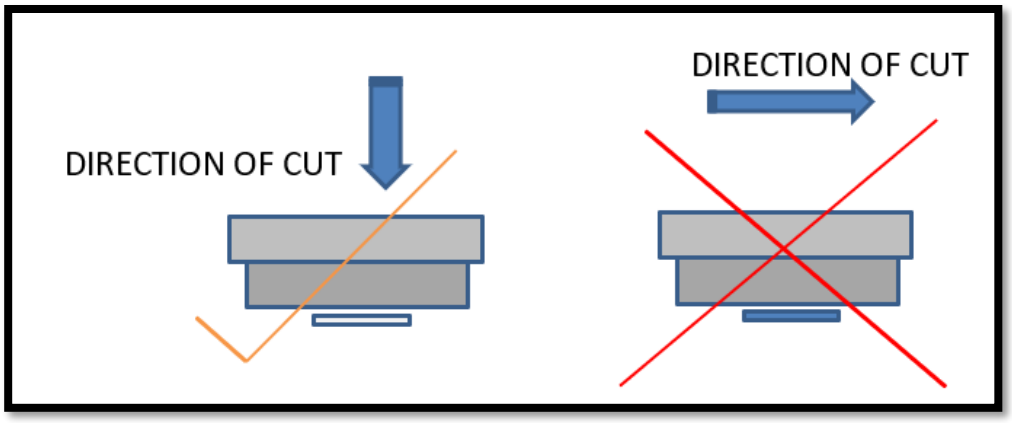


Figure 46. Probe Cutting Direction

Apply pressure to the blunt handle using hand pressure in a vertical, downward motion. The blade should simply CUT through the probe. **DO NOT USE A SLICING ACTION** to cut the probe tip as this might damage the insulation coating.

After each area scan it may be necessary to refresh the probe surface. Cut the end of the probe as described above. Clearly the smaller the cut, the longer the lifetime of the probe.

Once the probe has been cut it can be assembled in the holder.

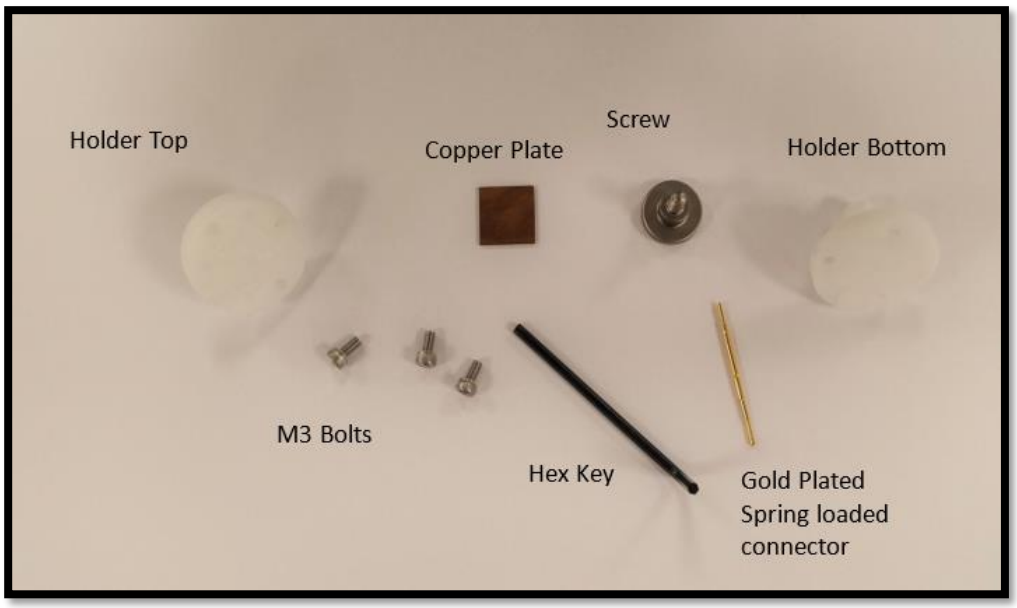


Figure 47. Probe Holder Pieces

The probe is shipped with a holder. Disassemble the holder as shown in the figure above.

The probe may be shipped with writing ‘UP’ on one side. This side is **NOT COATED** WITH INSULATION LAYER. If there is no marking, then it is quite easy to identify the correct side. The side with the Insulation coating is placed in contact with the sample since the thin coating ensures a small tip-substrate separation for better contrast imaging and higher resolution measurements.

To identify this side, gently rub a small area of the probe (at the electrical contact end since this end never contacts solution). Users will notice the Insulation coating start to delaminate. ***This identifies the coated side of the probe, and it is this side that contacts the sample***. It is recommended to mark this side for future reference.

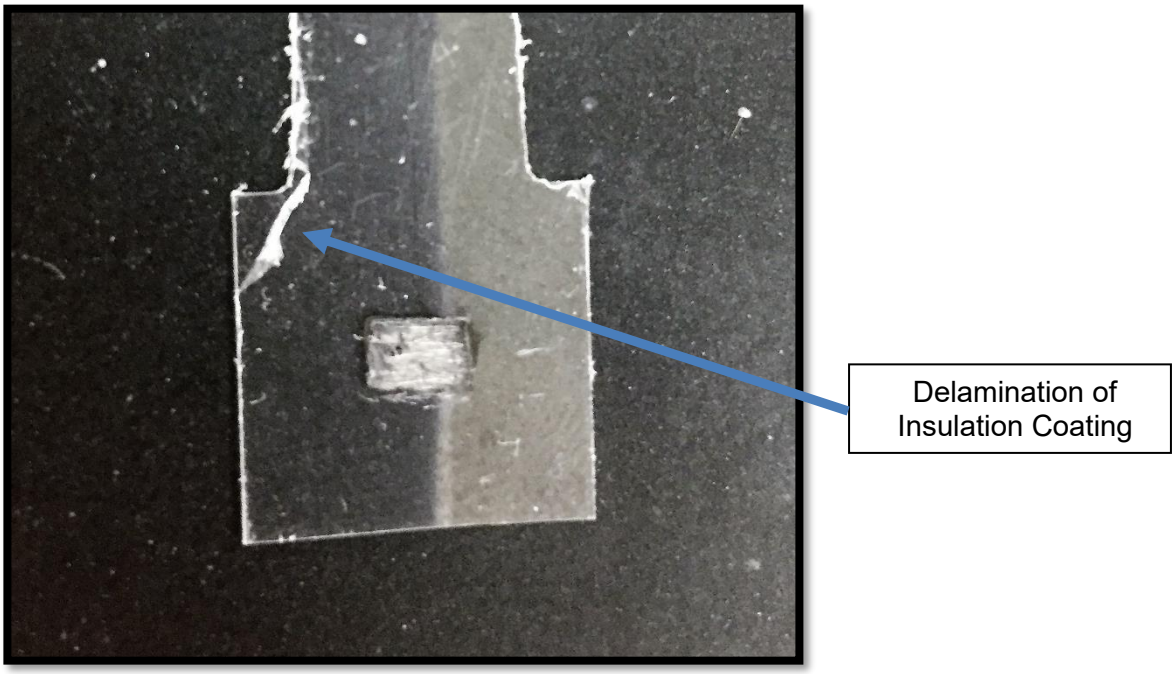


Figure 48. Delamination of Insulation Coating

NOTE It is very important to place the electrode in the correct orientation.

The following describes the correct procedure to load the probe into the holder.

First use the electrode holder top. Place the electrode into the recess with the insulation layer Coated side facing DOWN.

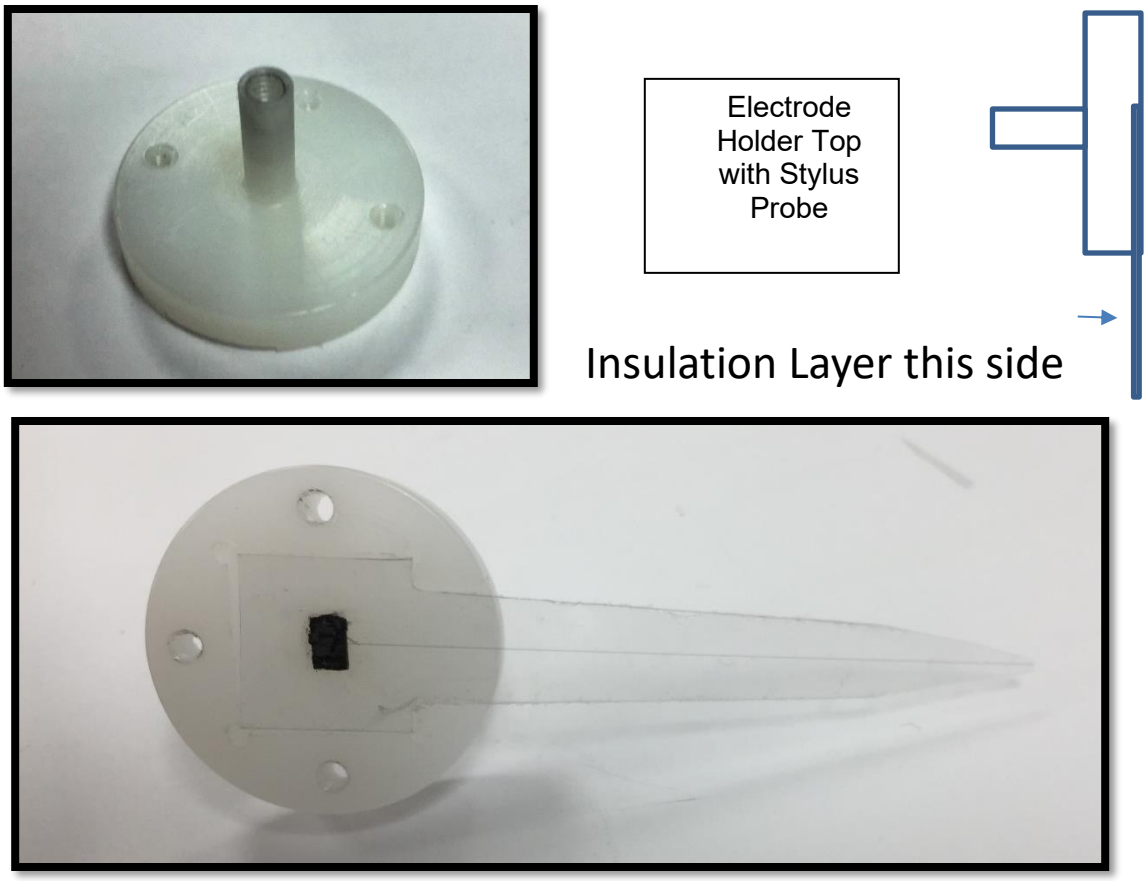


Figure 49. Electrode Loaded into Top Holder

Place the copper connection pad on top of the probe followed by the nylon housing and screw down using the three bolts provided.

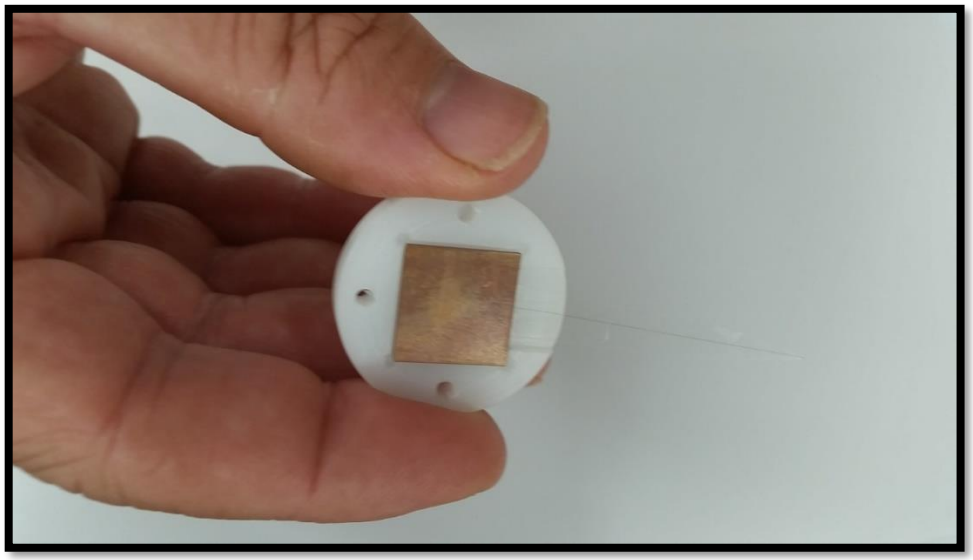


Figure 50. Copper Pad Place on the Probe

Place the gold-plated, spring-loaded connector through the central hole of the other electrode holder plate. This provides electrical connection to the probe itself. Insert the probe in the direction of the arrow.

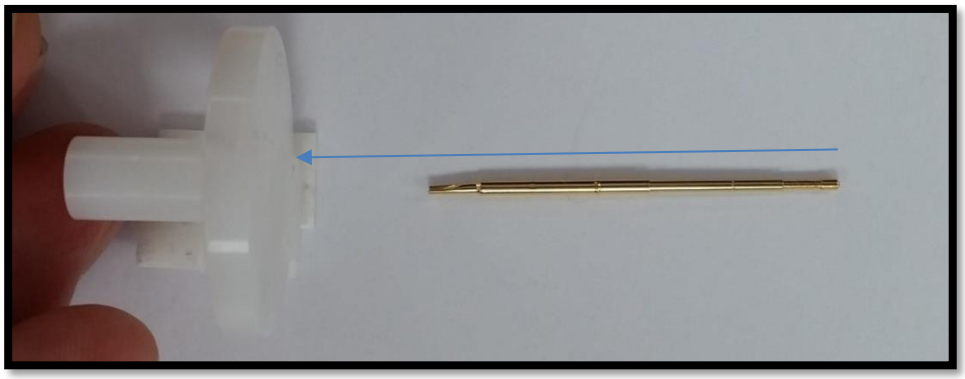


Figure 51. Place Gold-Plated Connector

The spring-loaded end needs to protrude as shown in the figure below. This will make a good electrical contact with the copper plate.

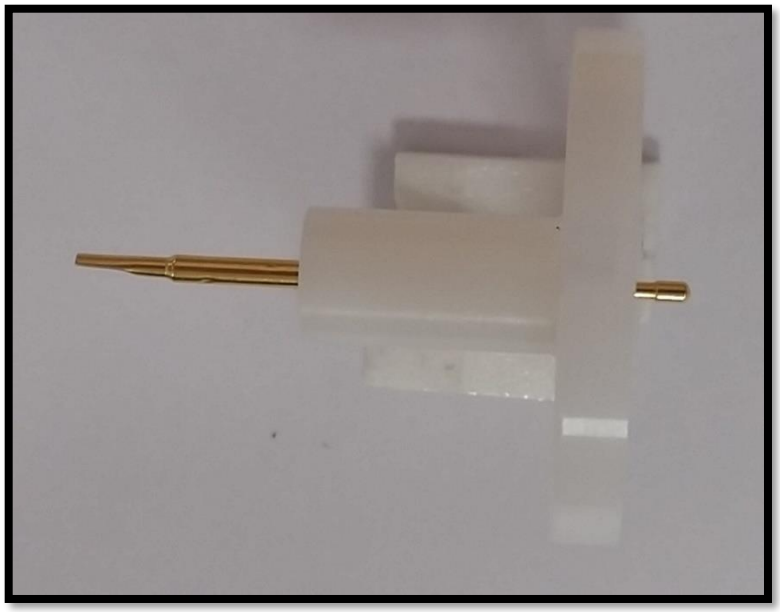


Figure 52. Connector in Position

Screw both plates together using the M3 screws provided.

Screw the holder onto the plate as shown using the bolt to securely fasten the holder to the rotary position stages.

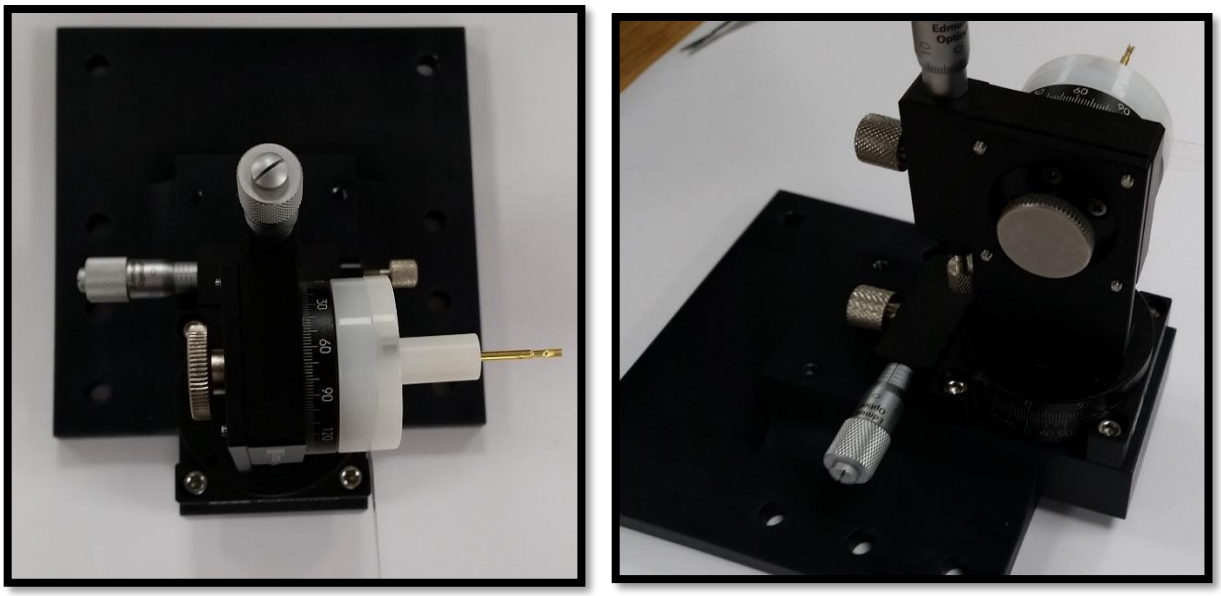


Figure 53. Holder Screwed onto Plate



Figure 54. Probe Mounted on Base Plate and Positioner Stage

5.3.2 Electrochemistry of the Probes

Once the probe is assembled it is recommended to check the electrochemical operation of the cell.

1. Make a solution of 1 or 2mMol Ferrocene Methanol in 0.1M KNO_3.
2. Use a suitable counter electrode and a quasi-silver reference electrode.
3. Manually position the electrode far away from the surface of the substrate so that users measure the bulk electrolyte response.
4. Record a CV from -0.2V to 0.4V at 25mV s^{-1}. Users should observe a scan similar to the one shown below.
5. It is now ready to start SECM experiments.

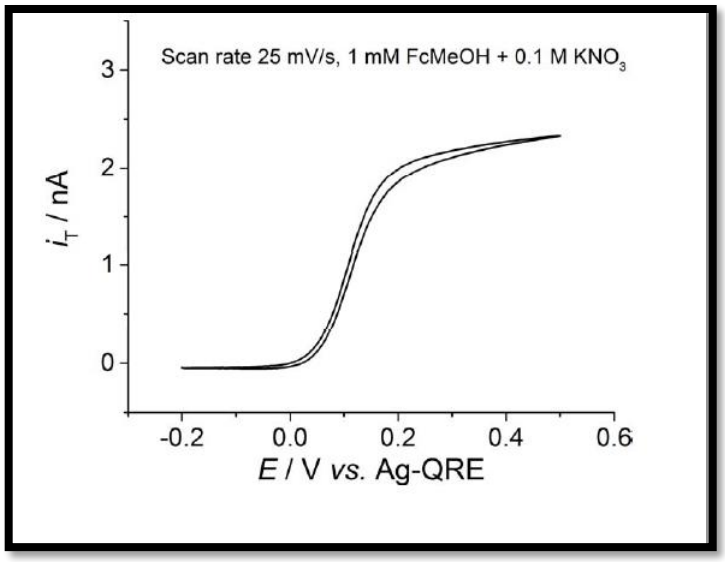


Figure 55. Cyclic Voltammogram of FcMeOH in 0.1M KNO_3

5.3.3 Using the Positioning Scales

The system makes use of rotary optical positioning scales. The probe angle can be adjusted either in the X and Y plane. For most studies, it is only necessary to adjust the X plane. The following section describes how to read the scale.

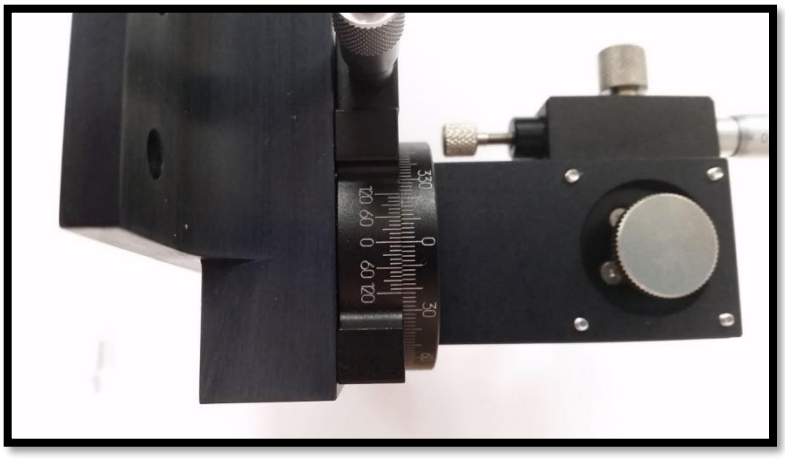


Figure 56. Rotary Optical Positioning Scales

1. Rotate the body of the holder until '0' on both scales match as shown above.
2. The division on the Right-Hand scale as shown is 10 degrees per major division and 2 degree per minor division.
3. To set the tilt angle, rotate the holder in a counterclockwise direction. In the example below read the displacement of the probe holder from 0 to determine the probe angle. In this case, the probe had been rotated 360 – 20 = 340 degrees. **The probe will make a 20-degree angle with the surface.**

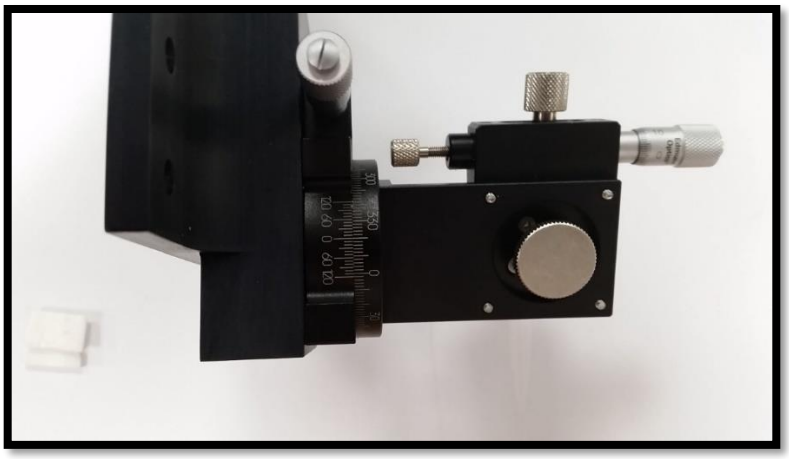


Figure 57. Example of Probe Angle

5.3.4 Positioning the Probe

It is important to understand the prove movement during MOVEMENT and MEASUREMENT (i.e., when the probe approaches the surface and how it scans across the surface during electrochemical measurements). The following section discusses this.

When run in constant distance mode, the probes make permanent contact with the surface. Since the probes are flexible, they should only be operated in one scan direction only. This is automatically determined in software. This prevents the probe snagging on the substrate which would distort the image.

The probes approach the surface at an angle (unlike hard probes which approach the curve in the z direction). This ensures that when the probe touches the surface it does not snag or bend in the wrong direction. Once on the surface, the probe is then scanned in one direction which is determined by software. This is described below in the figure.

The probe approaches the surfaces at a user defined probe angle from an initial height (also termed the lift off height).

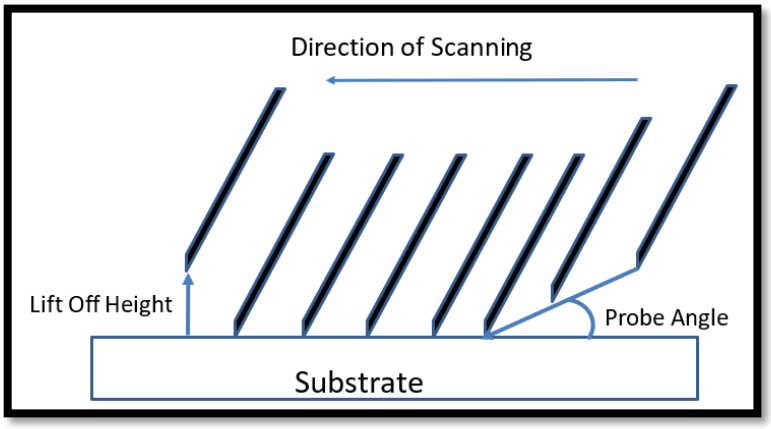


Figure 58. Probe Scanning Demo

The probe touches the surface of the sample at the user defined start position. Therefore, it is critical for the user to define the lift off height and the probe angle in order for the software to determine the correct position of probe once it has engaged the surface.

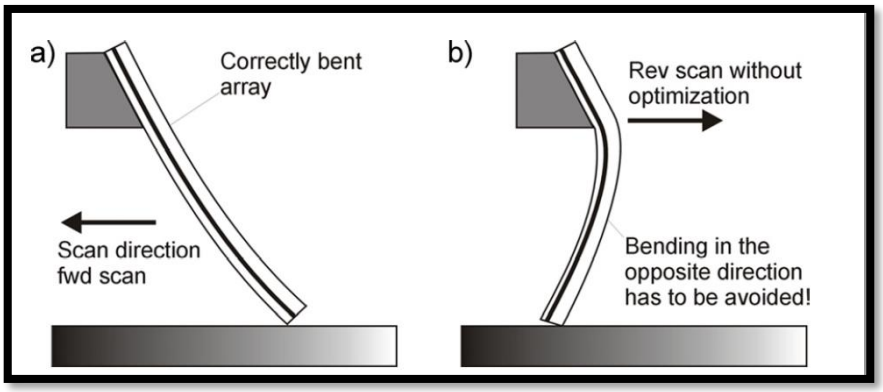


Figure 59. Correct Probe Bend Versus Incorrect Probe Bend

If the probe is scanned in the wrong direction, bending of the probe will occur and this must be avoided. To avoid this, the correct probe angle MUST be set to the correct value. This is covered in the next section.

The probe scans in either stepped or swept mode. In swept mode, it is recommended to use a speed of 25µm s^{-1}.

Once the probe reaches the end point of the line scan, the probe lifts off in the Z plane to the pre-defined lift off height. It then returns to the start position and increments its position in either X or Y to start the next line scan. An area scan is therefore constructed from a series of line scans (c.f. methodology used in constant height mode SECM).

5.3.5 Running Constant Distance Mode SECM Experiments

1. Select Soft Stylus Probe SECM from the drop-down list in the Hardware Requirements.

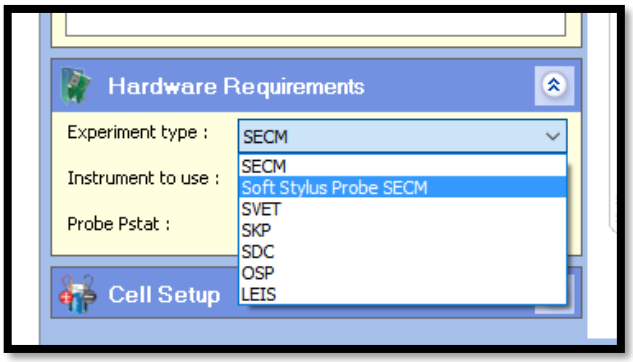


Figure 60. Select Soft Stylus Probe SECM

2. Open the manual control as shown and tick the 'soft probe' box.

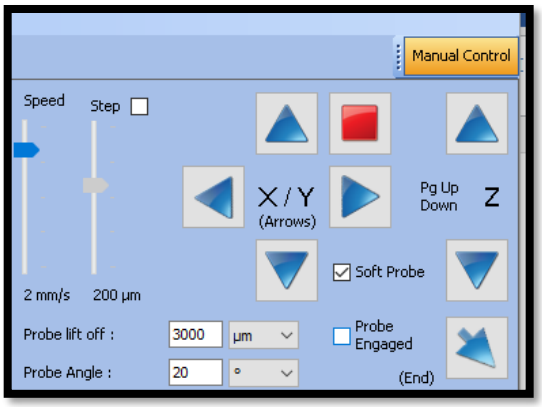


Figure 61. Manual Control Button

3. It is important to tell the software the angle that the probe will make with respect to the surface.
   To determine the input value, enter 360 – user required value.
   For example, if it is desired to apply a 20-degree touch angle, input 340 into the Probe Angle Box.

4. Probe lift off determines the distance the probe will travel at the end of the line scan. This height needs to be sufficient to clear all obstacles on its return journey to the start point.

5.3.6 Learning to Position the Probe Manually

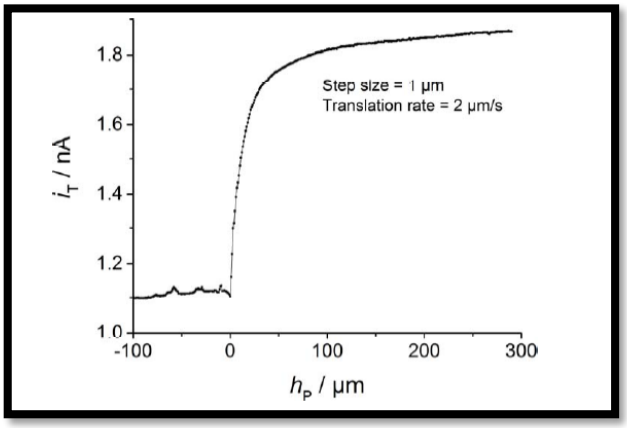


Figure 62. Current Versus Height

A useful experiment to help position the probe on the sample is to first ensure that the probe touches the sample (where the current is independent of the height ; $h_p < 0\mu m$). Then withdraw the probe in the Z direction and measure the current (see CV experimental details). It is easy to see the point at which the probe withdraws for the surface. Use the  key to place the probe on the surface. It will approach the surface at the angle specified in the probe angle text box.

5.3.7 Positioning Probe for Line and Area Scans

There are two methods to run Line and Area Scans:

- Probe already engaged at the start point before the test.

- Probe engages the sample at the start point defined in the step.

If there is uncertainty about where to position the probe on the sample using the X, Y, and Z settings, then placing the probe on the surface BEFORE beginning line or area scans is a useful feature in software. Position the probe using the manual control buttons and when the surface has been engaged at the start point, highlight the PROBE ENGAGED box in the manual.

The alternative is to run the scan without the probe engaged and allow the software to place the probe at the points defined in the step.

Using the probe successfully will require some practice, especially with respect to the placement of the probe.

5.4 Example Area Scan Setup

An example of the scan set-up for an area scan is presented below. It assumes that the PROBE is already engaged. It is recommended to use the probe engaged feature whilst becoming familiar with the system controls. The most critical parameter is to set the X parameter as a NEGATIVE VALUE. This ensures that the probe scans from RIGHT to LEFT – which allows correct movement without snagging.

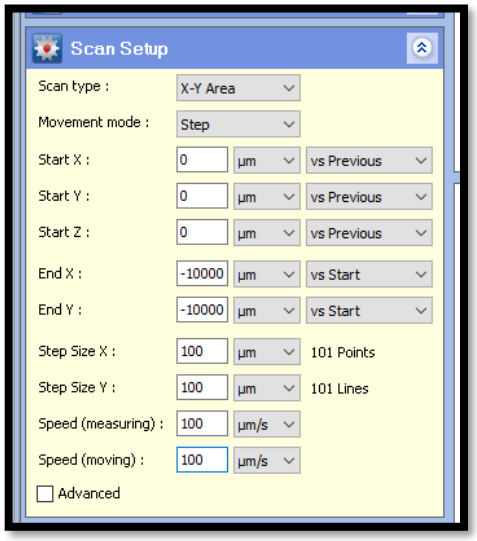


Figure 63. Scan Setup

6. VersaSCAN LEIS (VSC-LEIS)

The VersaSCAN LEIS is a Localized Electrochemical Impedance Spectroscopy (LEIS). It requires VSC-BASE and VSC-LEIS. It is recommended to use VSC-LCELL and VSC-CAM.

6.1 LEIS Technique Overview and Introduction

The Localized Electrochemical Impedance Spectroscopy (LEIS) uses a dual wire to measure potential field gradient drop in solution. A VersaSTAT 4A Potentiostat with Differential Auxiliary Voltage Input is used to apply the AC signal and measure the response in VSC-LEIS. The V4A applies a global AC voltage to the sample, and processes the response measured by the probe and electrometer using the Diff Aux Volt In. The applied AC voltage generates a corresponding AC current. Due to the differing localized activity of the sample, different localized currents at the surface of the sample.

The local current exists in solution of some determined conductivity. By measuring the voltage-drop or difference between the two elements (ΔV) over a known distance (cm) and a measured conductivity (S/cm); the system can determine the localized current (i). The VersaSCAN uses an Electrometer to gain the voltage-drop between the two elements of the probe. This measured voltage in solution is routed to the Diff Aux Volt In and used to determine AC current response. The ratio of the localized current and applied voltage gives the localized electrochemical impedance (Z).

In discussions of LEIS, it is important to understand the different voltages in the system. The V4A with Diff Aux Volt In applies an AC voltage to the sample; the VersaSCAN determines current by measuring the voltage in solution.

It is useful to acquire data in different modes: “Single Frequency” measures impedance at different probe positions and generates a data map; “Frequency Sweep” measures impedance at a single probe position at different frequencies.

6.2 Applications

LEIS provides high-information content results to similar applications that benefit from bulk, traditional EIS measurements, such as the study of coatings and corrosion of bare metals. LEIS benefits from the ability to use frequency as a tool to investigate distinct electrochemical processes.

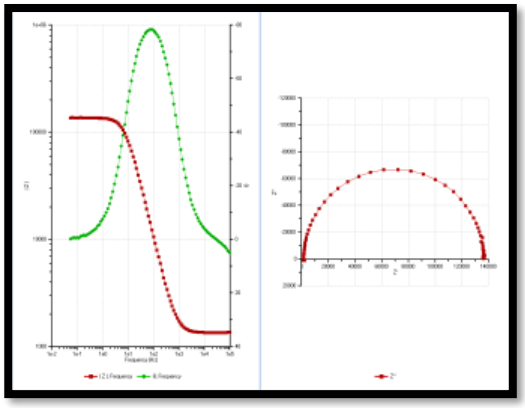


Figure 64. LEIS Dummy Cell Response - Frequency Sweep

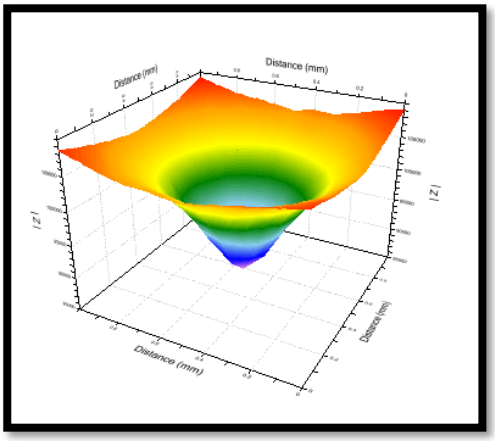


Figure 65. Results from Gold Point-In-Space in Tap Water with 100mV Applied

6.3 VSC-LEIS Packing List

Table 9. VSC-LEIS Packing List

Description	Ametek PN	Quantity (Each)
Potentiostats		
VersaSTAT 4A-400*	VERSASTAT 4A-400VSD	1
Connection BNC Terminator 50 Ohm	773280	1
Control Box		
VersaSCAN System Control Box*	244118-PT	1
Electrometer and Mounting Hardware*		
VersaSCAN Electrometer*	224077	1
SHCS M3X0.5-25mm	233848	4
VersaSCAN Spacer	224134	1
SCR M3x0.5-20mm	233788	4
Probes and Electrodes		
VersaSCAN LEIS Probe	224114	1
VersaSCAN Counter Electrode	224198	1
LEIS Dummy Cells		
VersaSCAN Gold Wire Test Sample*	224116	1
VersaSCAN Dummy Cell	224211	1
Connectivity and Power Cables*		
Extension Cord	803937	2
Cable, BNC-SMC	233925	1
Cable, Data DB-25 – DB-37, M/F	1116426	1
Cable, Data DB37, M/M	1107199	1
Cable, BNC-BNC	SC0033	1
Cable, Trigger, SMA-BNC, 1m	1116486	1

*Indicates that item is used on multiple techniques and will not be duplicated in shipment.

6.4 Cable Connections for VSC-LEIS

> **NOTE** If the system has TWO motion controller boxes, please refer to Appendix 1 for set-up diagrams.

The diagrams are additionally available as part of the “Setup” of each experiment.

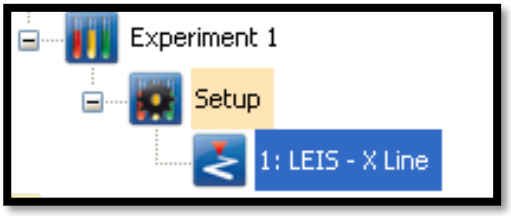


Figure 66. LEIS Setup Diagram

Cable Connections for a Potentiostatic controlled sample are below.

This assumes that connections for the positioning system are already in place for the motors and encoders. As well as the communication cable: Ethernet for motion controllers and computer; USB for the V4A. The drivers for the V4A must be installed as well.

Table 10. Cell Connections for LEIS

OUT	IN	CABLE
Motion Controller (XYZ)	System Box (XYZ)	25-PIN to 37-PIN and 37-PIN to 37 PIN
Top of Electrometer	System Box (Electrometer)	9-Pin Male to Male
Side of Electrometer	Diff. Sync ADC (+) of V4A-400VSD	SMC-to-BNC
Trig on System Box	Trig on Motion Controller	BNC-to-SMA

The V4A is connected to the electrochemical cell as typical.

- Working (Green) + Sense (Grey) to sample
- Reference (White) to the Reference electrode (Counter in a 2-electrode experiment)
- Counter (Red) to the Counter electrode - Circular Pt Counter is supplied

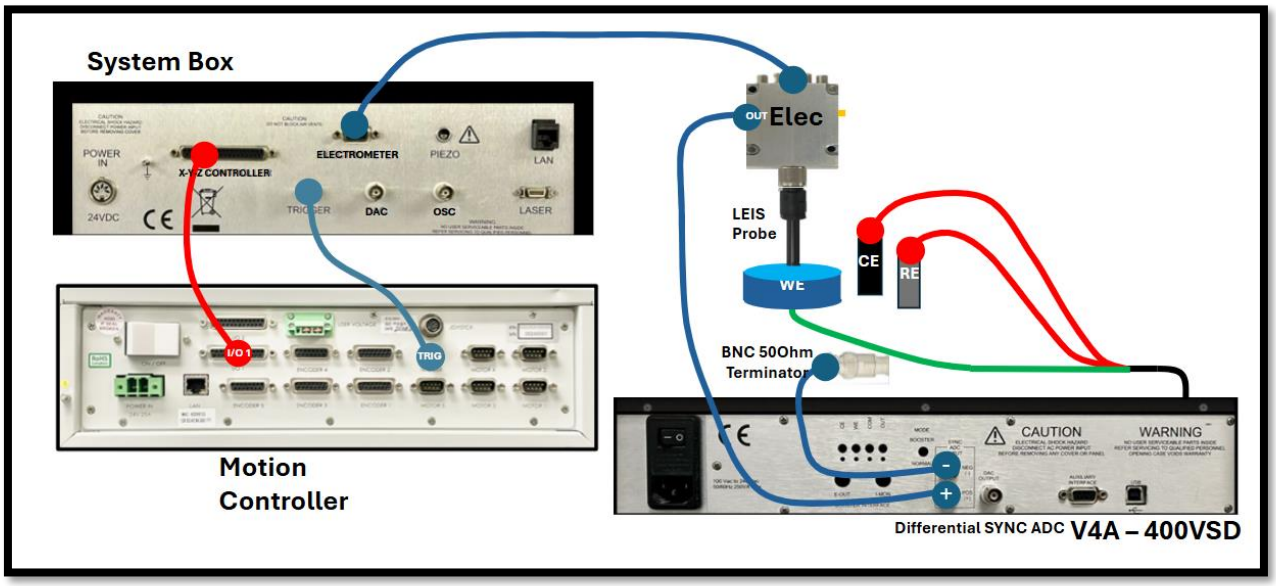


Figure 67. LEIS Connections

6.5 Software Control for VSC-LEIS

6.5.1 Comments

Any comments that need to be stored with the data file can be entered into this field.

Please note that all the Scan and Measurement parameters from the experiments are already stored in each data file, so those are not necessary to be entered here.

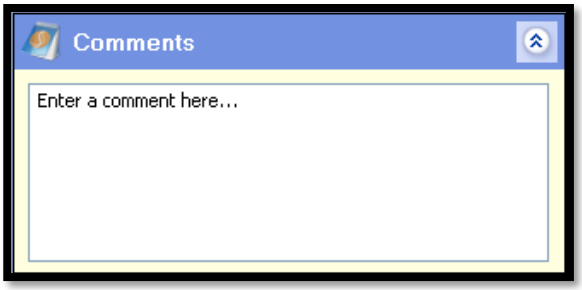


Figure 68. Software Comments Field

6.5.2 Conditioning

The Conditioning tab allows the user to set the time for the system to be delayed before any measurement in the Step is started. Note this programmed delay occurs once before the experiment starts. The Measurement & Delay window allows other specific delays between each line and between each point to be programmed. The units for the description of time are also selectable.



Figure 69. Software Conditioning Field

6.5.3 Scan Setup

Scan Setup is a generic tab that has a familiar look and feel in all the techniques.

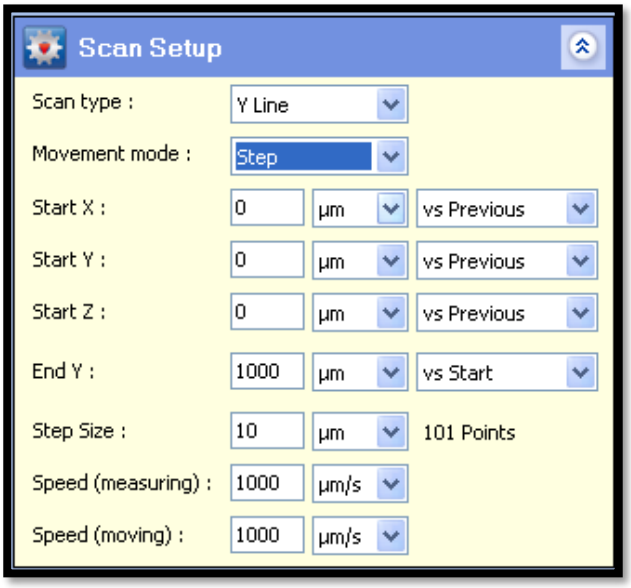


Figure 70. Software Scan Setup

6.5.3.1 Scan Type

The "Scan type" allows the user to define if the experiment is going to be executed in a single line axis or in an area as a series of line experiments. "X Line" would be a single line of data in X, while maintaining a constant Y and Z position. "Y-Line" scans in Y as "Z Line" scans in Z.

"XY Area" will map an Area in the XY plane. This is accomplished by a series of X scans at different Y positions. Data acquisition occurs as the probe moves from Start X to End X (e.g., for -X to +X this is left to right).

"Point" will execute the experiment without moving the probe.

6.5.3.2 Measurement Mode

In LEIS, VersaSCAN acquires data in STEP Mode because of the requirement for calculations of impedance.

STEP Mode will oversample and average the data. The probe moves to a given location and remains in that location for the measurement duration. Then, it moves stepwise to the new location (1 x Step Size; here 10 microns). Oversampled data collection again occurs at the new location. Data is averaged and reported. This oversampling and averaging process reduces the noise in the experiment but increases the duration of the experiment.

Other techniques have the option of SWEEP Mode. SWEEP Mode will acquire data while the probe is moving. Data is not oversampled, which decreases the overall duration of the experiment, but may affect data quality. Time Constant of the signal chain should be considered when setting the Sweep parameters, as the probe's position is changing as data is coming from the signal chain.

6.5.3.3 Start X/Y/Z

In this field, the user defines the specific position that the experiment starts.

This can be set as "vs. Previous" or "vs. Absolute".

"vs. Previous" will allow the probe to use its current position as the origin point. In this example, 0/0/0 vs. Previous starts the experiment from the probe's current position.

"vs. Absolute" will use the known extreme position in order to keep an absolute reference grid from which positions are specified. 0/0/0 would be the far left (-X) ; back (-Y) and down (-Z).

6.5.3.4 End vs. Start

In this field, the user defines the location where the experiment is terminated.

The "Start" and "End" define the distance or area over which the experiment is performed.

The dimensions of the Scan Area should be considered when Aspect Ratio of the data of the end-result.

6.5.3.5 Step Size

This field defines the data point density. A data point is acquired and recorded at every Step size. High resolution experiments would require small step size as one component.

In Area Scan, the user can define different densities in X and Y. Pixels do not have to be squares (equal X and Y) but it is recommended and set as the default.

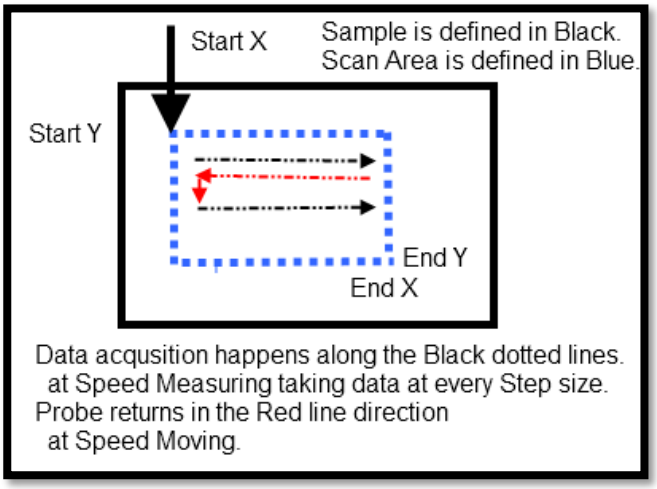


Figure 71. Area Scan

6.5.4 Measurement & Delay



Figure 72. Software Measurement and Delay

6.5.4.1 Line Delay

The Line Delay allows the user to program a set time delay between each line of data acquisition. This is helpful when waiting for motion in the electrolyte (convection) caused by the return scan to settle. Additionally, highly filtered data (long Time Constants) can benefit from using this to allow the data to exit the filter.

6.5.4.2 Measure Delay

This complementary delay is at every point during the scan.

Conditioning: Delay is at the start of the experiment.

Line Delay: Delay is at the start of each line.

Measure Delay: Delay is at each data point.

6.5.5 Potentiostat Setup

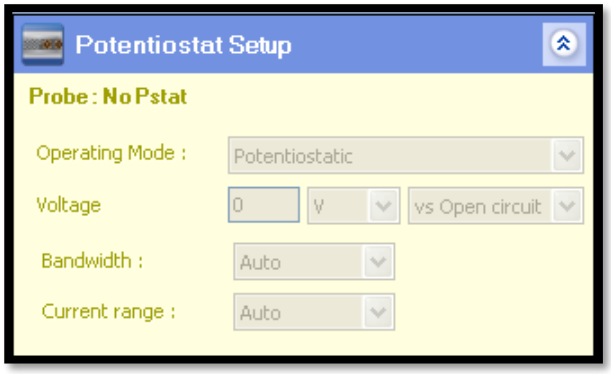


Figure 73. Software Potentiostat Setup

This window sets the configuration for the DC settings of the potentiostat.

Operating Mode: This parameter allows the user to select between applied potential (Potentiostatic) and applied current (Galvanostatic) control.

Voltage (or Current): This parameter allows the user to set the DC Bias on which the AC signal is applied. The most common configuration is to run the system with no external DC Bias applied: either 0V vs. Open Circuit or 0 Amps.

Bandwidth: This is a parameter that accounts for the speed at which the potentiostat can apply, adjust, and measure the signals and responses. Higher speeds allow access to higher frequencies in LEIS; however, lower speeds increase the stability of the system.

If the system is rolling off, the user can select a higher Bandwidth speed. If the system is oscillating, the user can select a lower Bandwidth speed.

Current Range: This parameter allows the user to select the current ranges of the potentiostat available for the particular measurement. This can be the entire range ("Auto") or a limited range, including even a single current range.

6.5.6 Impedance Setup

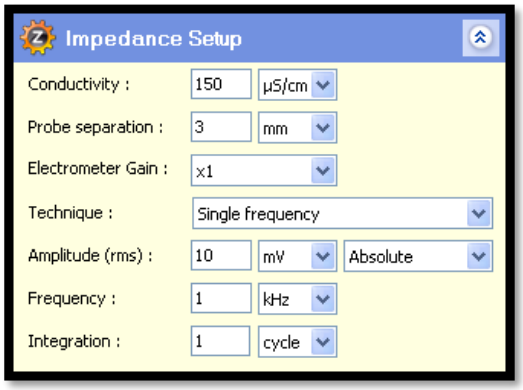


Figure 74. Software Impedance Setup

This window sets the configuration for the AC settings for the measurement.

Conductivity: The solution conductivity is going to affect the measure of the impedance in LEIS. The system will measure the voltage-drop in solution.

$$I_{local} = \frac{\kappa V_{probe}}{d} \qquad Z_{local} = \frac{V_{applied}}{I_{local}}$$

This parameter allows the user to input the conductivity for quantitative measurements and those that compare samples in different system test environments.

NOTE This parameter greatly impacts resolution of the measurement, consult other literature for a detailed explanation.

Probe Separation: The LEIS probe is a dual-element probe. Since this is a voltage-drop measurement, this parameter allows the user to adjust for spacing between the 2 elements in the probe. The standard probe (P/N 224114) has a spacing of 3 mm between its two measurement elements – the ring and the pin.

Electrometer Gain: The Electrometer measures the response of the probe. This analog measurement can have gain applied by a pre-amplifier circuit. The available gain selections are in decades from 1x to 10,000x. The higher the gain selection the lower the bandwidth; therefore, for the highest frequency of interest the 1x Gain is recommended.

Technique: There are multiple modes to acquire LEIS data.

Frequency Sweep: Data will be acquired over a range of frequencies.

Single Frequency: Data will be acquired at a single specific frequency.

Amplitude: This parameter allows the user to adjust the size of the AC perturbation that is applied to the sample. In a linear system, the larger the perturbation applied to the sample, the larger the response. Larger responses can be more easily measured with less Gain. However, if perturbations become too large, the system may go non-linear in its response. This is true for bulk, traditional EIS systems as well and must be considered.

Frequency: This parameter allows the user to set the frequency of the AC perturbation. In a scanning experiment, this is a fixed frequency.

In a stationary experiment, the user can select an Initial and Final frequency. Additional selections on Linear and Logarithmic spacing and data point density are then available.

Integration: This parameter allows the user to select the number of cycles of the EIS algorithm to process before the result is calculated. A longer integration cycle will increase data quality but impact the duration of the experiment. This may have a negative impact on throughput as well as changing response in an active system.

6.6 VSC-LEIS System Test Procedure for LEIS Dummy Cell

This document assumes that the system has been assembled per instructions in the accompanying guides.

1. Mount and cable the VersaSCAN system as described in the manual.

This assumes that connections for the positioning system are already in place for the motors and encoders as well as the communication cable, Ethernet for the motion controllers and computer, and USB for the V4A. The drivers for the V4A must be installed as well.

Table 11. LEIS Cable Connections for LEIS Dummy Cell

OUT	IN	CABLE
Motion Controller (XYZ)	System Box (XYZ)	25-PIN to 37-PIN and 37-PIN to 37 PIN
Top of Electrometer	System Box (Electrometer)	9-Pin Male to Male
Side of Electrometer	Diff. Sync ADC (+) of V4A-400VSD	SMC-to-BNC
Trig on System Box	Trig on Motion Controller	BNC-to-SMA

2. Use the Manual Control in the VersaSCAN software to position the Electrometer in its maximum Z position as high as possible.

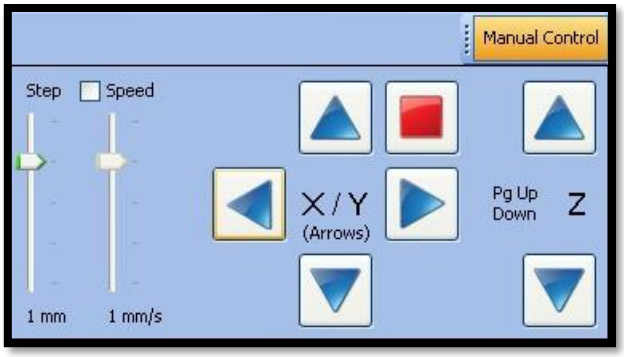


Figure 75. Manual Control Settings

3. Mount the cable from the VersaSCAN Dummy Cell (P/N 224211) to the Electrometer (P/N 224077).

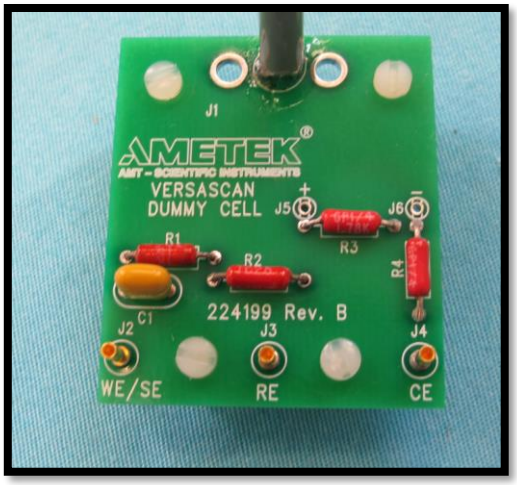


Figure 76. VersaSCAN Dummy Cell

4. Connect the V4A Potentiostat to the electrodes in the cell.

   a. Working (Green) + Sense (Grey) together to “WE” post on the dummy cell board.
   b. Reference (White) to the “RE” post on the dummy cell board.
   c. Counter (Red) to the “CE” post on the dummy cell board.

5. In the VersaSCAN software select the menu option “File” and select “New Project”. Within the “Project” an Experiment is created. Insert a Step of the Localized Electrochemical Impedance Spectroscopy (LEIS).

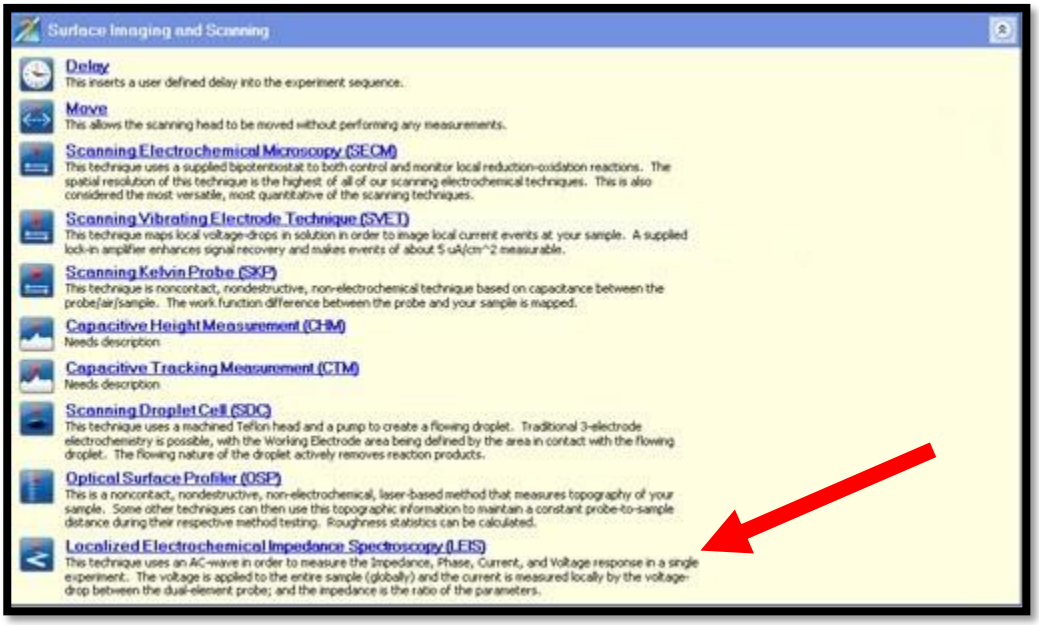


Figure 77. Surface Imaging and Scanning

The file Setup window for the LEIS Step will be displayed. See VersaSCAN LEIS Operator’s Guide for a detailed explanation of all test parameters.

6. Select Scan Type: Point - The starting position parameters are not relevant for this experiment.

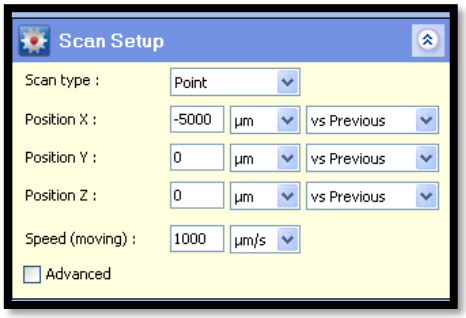


Figure 78. Scan Setup – Select Point

7. The new experiment now needs to be configured. The LEIS experiment Potentiostat and Impedance Setup window will be displayed. See the VSC-LEIS Users Guide for details on the controls.

   Suggested parameters for the LEIS Dummy Cell.

   Potentiostat Setup:

   a. Operating Mode: Potentiostatic

   b. Voltage: 0 Volts vs. Open Circuit

   c. Bandwidth: Auto

   d. Current Range: Auto

   Impedance Setup:

   a. Conductivity: Use 150µS/cm

   b. Probe Separation: 3 mm

   c. Electrometer Gain: 1x

   d. Technique: Frequency Sweep, 100 kHz to 50 mHz

   e. Amplitude: 100 mV rms vs. Absolute

8. Run the experiment. Select "Run".



Figure 79. Run Icon

NOTE No data will appear on the screen until the experiment is completed. Users may hear the VersaSTAT 4A clicking through its ranges.

9. The screenshot below shows the typical data obtained from the test experiment.

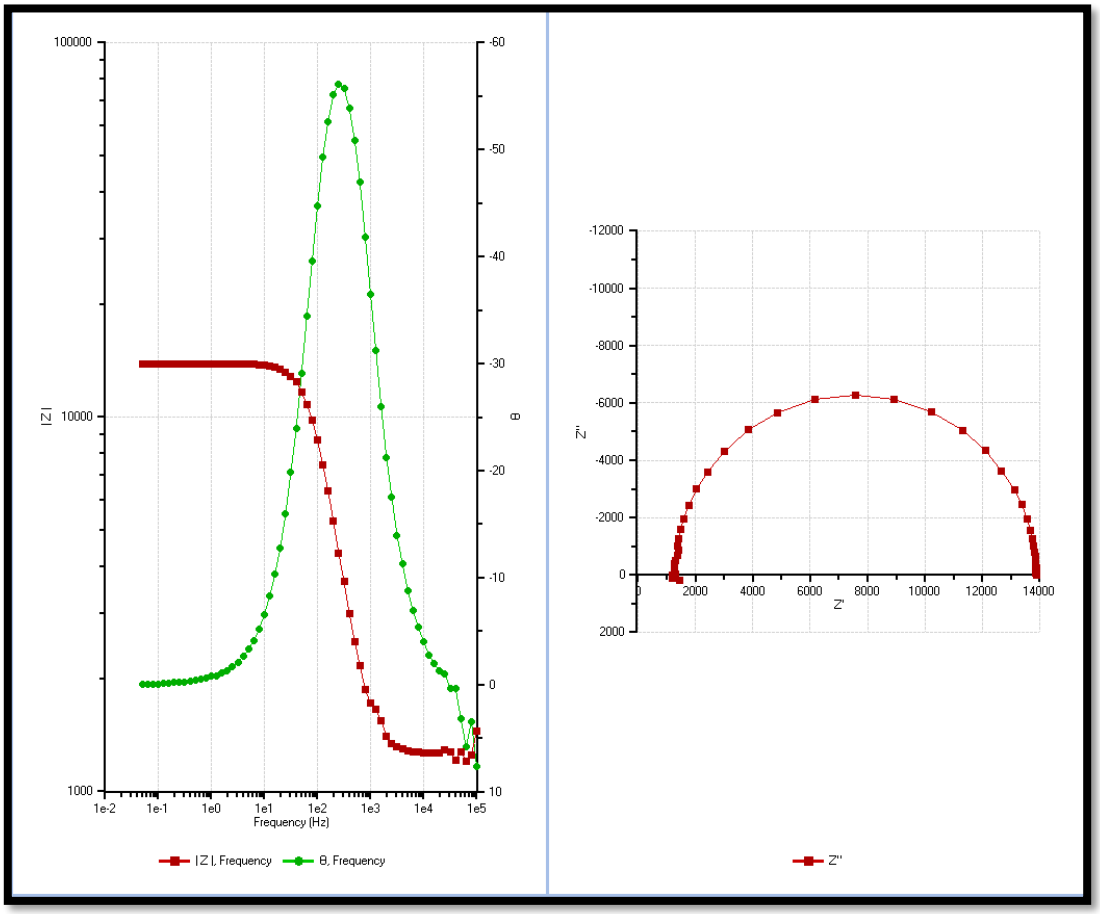


Figure 80. LEIS Dummy Cell Test Results

6.7 VSC-LEIS System Test Procedure for Gold Wire Test Sample

This document assumes that the system has been assembled per instructions in the accompanying guides.

NOTE The VSC-LCELL is highly recommended for LEIS work. The geometry of the VSC-MLCELL and the circular PT Counter Electrode leaves a very small scan area available.

1. Mount and cable the VersaSCAN system as described in the manual.

   This assumes that connections for the positioning system are already in place for the motors and encoders, as well as the communication cable, Ethernet for the motion

controllers and computer, and USB for the V4A. The drivers for the V4A must be installed as well.

Table 12. LEIS Cable Connections for Gold Wire Test Sample

OUT	IN	CABLE
Motion Controller (XYZ)	System Box (XY)	25 Pin to 37 Pin and 37 Pin to 37 Pin
Top of Electrometer	System Box (Electrometer)	9-Pin Male to Male
Side of Electrometer	Diff. Sync ADC (+) of V4A-400VSD	SMC-to-BNC
Trig on System Box	Trig on Motion Controller	BNC-to-SMA

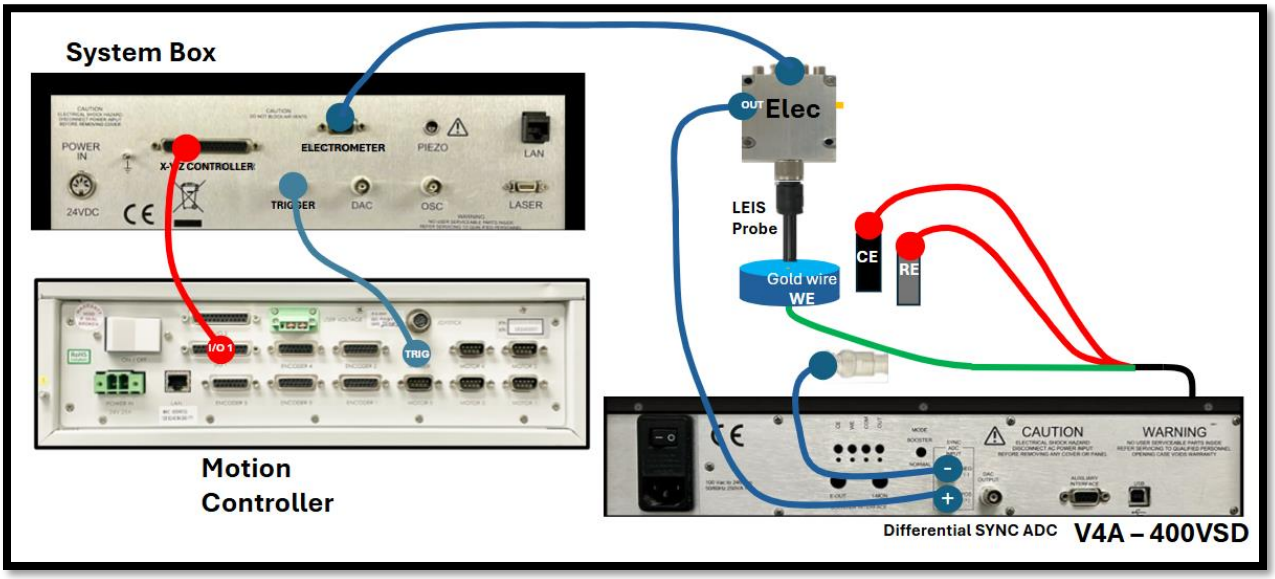


Figure 81. LEIS Setup for Gold Wire Test Sample



Figure 82. V4A-400VSD Differential Sync ADC Connections

2. Mount the VersaSCAN Gold Wire Test Sample (P/N 224116) into the cell and level it.

3. Fill the cell with suitable electrolyte. Drinking water with a typical conductivity of 150µS/cm is suitable for the test sample. It is recommended that users check the conductivity with a conductivity meter. The electrolyte level should be such that all the electrodes are immersed in the liquid.

4. Mount the LEIS probe (P/N 224114) into the Pt wire Counter Electrode (P/N 224198).



Figure 83. LEIS Probe Mounting in the PT Wire Counter Electrode

5. Connect the LEIS probe assembly to the Electrometer (P/N 224077).

6. Connect the V4A Potentiostat to the electrodes in the cell.
   a. The V4A is connected to the electrochemical cell as typical.
   b. Working (Green) + Sense (Grey) to sample
   c. Reference (White) to the Reference electrode (Counter in a 2-electrode experiment)
   d. Counter (Red) to the Counter electrode. Circular Pt Counter is supplied.

7. Use the Manual Control in the VersaSCAN software to position the tip of the LEIS probe such that it is aligned above the gold wire of the test sample by approximately 100 micrometers. The Probe tip should be aligned precisely in the X&Y planes. Great care should be taken to avoid the tip of the probe from touching the sample. The probe tip is easily damaged by any contact. However, it should be noted that it is critical for successful operation of the technique that the probe to sample distance be as small as possible. This directly affects the spatial resolution of the technique, by virtue of geometry.

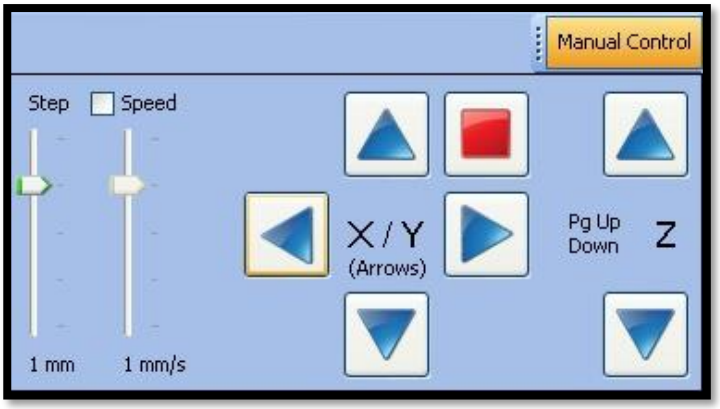


Figure 84. Manual Control Settings

8. In the VersaSCAN software select the menu option "File" and select "New Project". Within the "Project" an Experiment is created. Insert a Step of the Localized Electrochemical Impedance Spectroscopy (LEIS).

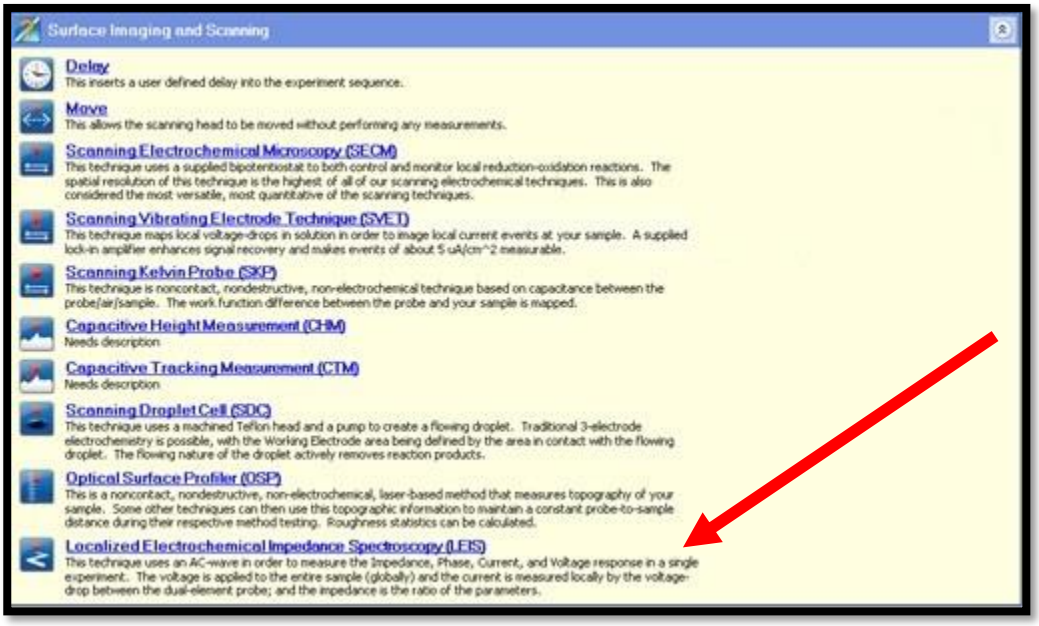


Figure 85. Surface Imaging and Scanning

The file Setup window for the LEIS Step will be displayed. See VersaSCAN LEIS Operator's Guide for a detailed explanation of all test parameters.

9. If the LEIS probe is positioned directly over the gold wire, these parameters will cause a 10 mm Line Scan in X with the gold being centered.

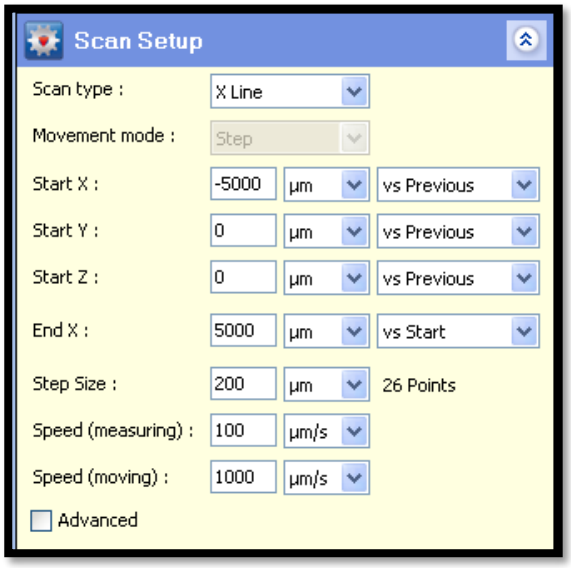


Figure 86. Scan Setup

10. The new experiment now needs to be configured. The LEIS experiment Potentiostat and Impedance Setup window will be displayed. See the VSC-LEIS Users Guide for details on the controls.

    Suggested parameters for the Gold Wire Test Sample.

    Potentiostat Setup:
    a. Operating Mode: Potentiostatic

    b. Voltage: 0 Volts vs. Open Circuit

    c. Bandwidth: Auto

    d. Current Range: Auto

    Impedance Setup:
    a. Conductivity: Use the measured conductivity of the electrolyte, e.g., 150 µS/cm

    b. Probe Separation: 3 mm for standard LEIS probe, P/N 224114

    c. Electrometer Gain: 1x

    d. Technique: Single Frequency, 1 kHz

    e. Amplitude: 100 mV rms vs. Absolute

11. Run the experiment. Select “Run”. By starting the experiment with the suggested parameters, the probe will move -2 mm to the left and -1.5 mm in Y; then start at 4 x 3 mm experiment. Each line of the scan is completed, and the data is plotted on the line graph and on the area contour map.



Figure 87. Run Experiment Icon

12. The screenshot below shows the typical data obtained from the test experiment.

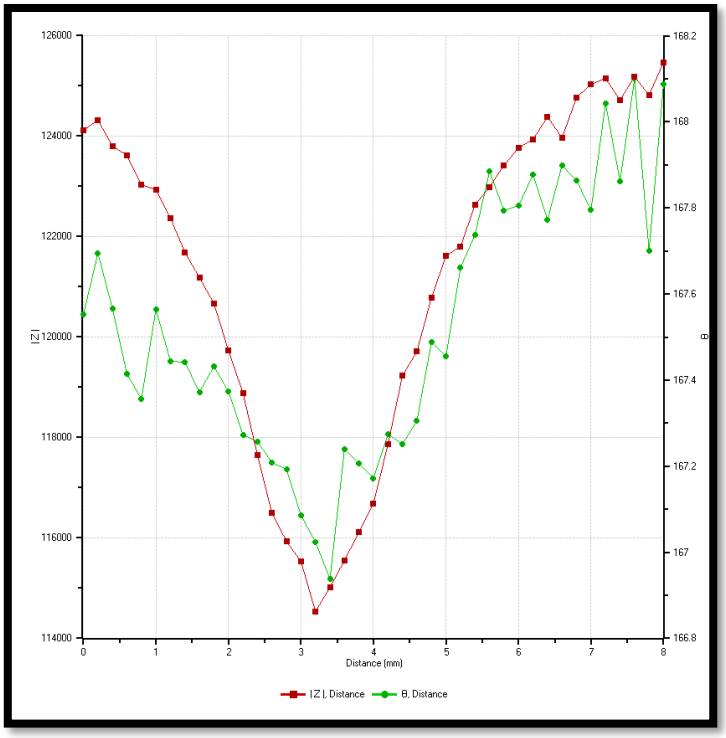


Figure 88. Gold Wire Test Sample Results

NOTE The impedance results decrease over the gold wire.

13. After successfully running a Line Scan experiment in LEIS in the X-direction, users position the probe directly over the gold in X, by moving it to the position of lowest impedance. Then, either a Line Scan in Y or an Area Scan can be executed.

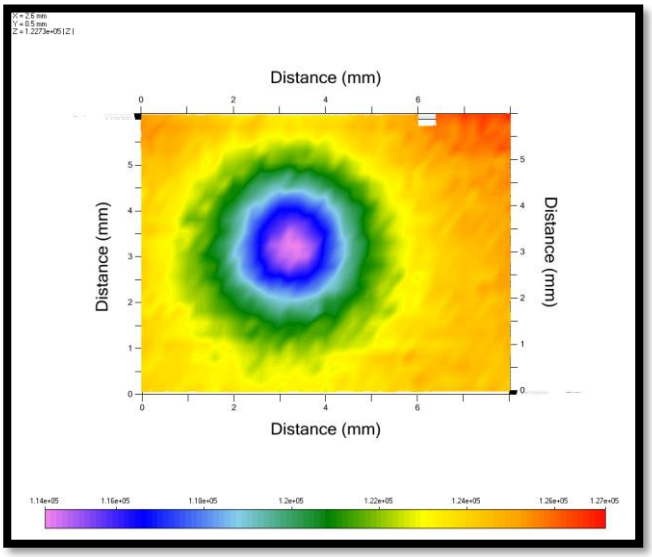


Figure 89. Probe Scan Results

7. VersaSCAN SVET (VSC-SVET)

The VersaSCAN SVET is a Scanning Vibrating Electrode Technique (SVET). It requires VSC-BASE and VSC-SVET. It is recommended to use VSC-CAM and VSC-LCELL or VSC-mLCELL.

7.1 SVET Technique Overview and Introduction

The Scanning Vibrating Electrode Technique uses a single wire to measure potential field gradient drop in solution. This voltage drop is a result of local current at the surface of a sample. Measuring this gradient in solution images the current at the sample surface. Current can be naturally occurring from a corrosion or biological process, or the current can be externally controlled using a galvanostat. A piezo unit vibrates the probe in Z-direction (axis perpendicular to the sample). The amplitude of vibration may be only tens of microns peak-to-peak. This small vibration provides a very small voltage to be measured.

Therefore, the response (signal + noise) at the probe is then amplified by the electrometer. The gained output of the electrometer is then input to a Lock-in Amplifier. This, in turn, uses a phase detector along with a Reference at the same frequency of vibration to extract the small AC signal from the entire measured response. The VersaSCAN capitalizes on Ametek's industry-leading Noise Characteristics of the Signal Recovery 7230 Lock-in Amplifier to provide superior measurement of these small signals. The voltage is recorded, and the probe is repositioned. A data map results as voltage versus position are displayed.

7.2 Applications

A key application of SVET is to study corrosion process of bare metals. These metals could be galvanic couples, or these fields could occur from local non-uniform corrosion events, such as pits or crevices.

Time-lapse experiment series provide the capability to watch the corrosion events happen - as different areas passivate and activate. Additionally, there are many applications and references for the use and results of SVET to study biological systems.

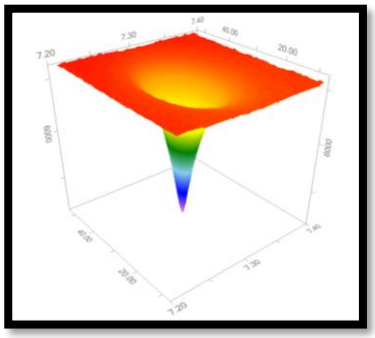


Figure 90. Results from Gold Point-in-Space in Tap Water with -10µA Applied

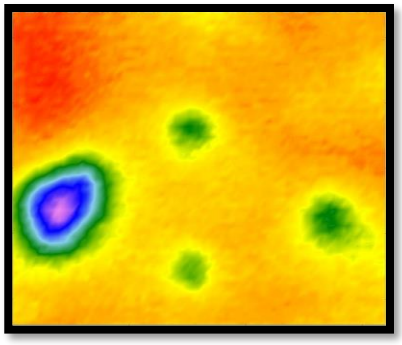


Figure 91. Results from Bare Metal Corrosion Process

7.3 VSC-SVET Packing List

Table 13. VSC-SVET Packing List

Description	Ametek PN	Quantity (Each)
Potentiostats		
Dual Phase DSP Lock-in Amplifier	7230-VS	1
VersaSCAN System Control Box*	224118-PT	1
Piezo Motion Unit*	233737	1
SCR M3x0.5-14mm SHCS 316ss	233792	2
Electrometer		
VersaSCAN Electrometer*	224077	1
SHCS M3X0.5-25mm	233848	4
Spacer		
VersaSCAN SDC Spacer	224134	1
SCR M3x0.5-20mm	233788	2
Probes and Electrodes		
VersaSCAN SVET Probe	224111	1
Test Sample		
VersaSCAN Gold Wire Test Sample*	224116	1
Connectivity and Power Cables*		
Extension Cord	803937	2
Cable, 9-PIN M/M	233973	2
Cable, Data DB-9 M/M	233918	1
Cable, Data DB-25 – DB-37, M/F	1116426	1
Cable, Data DB37, M/M	1107199	1
Cable, BNC-BNC	SC0033	3
Cable, Trigger, SMA-BNC, 1m	1116486	1

*Indicates that item is used on multiple techniques and will not be duplicated in shipment.

7.4 Cable Connections for VSC-SVET

> **NOTE** If the system has TWO motion controller boxes, please refer to Appendix 1 for set-up diagrams.

The diagrams are additionally available as part of the “Setup” of each experiment.



Figure 92. SVET Setup Diagram

Cable Connections for an Open Circuit controlled sample are below.

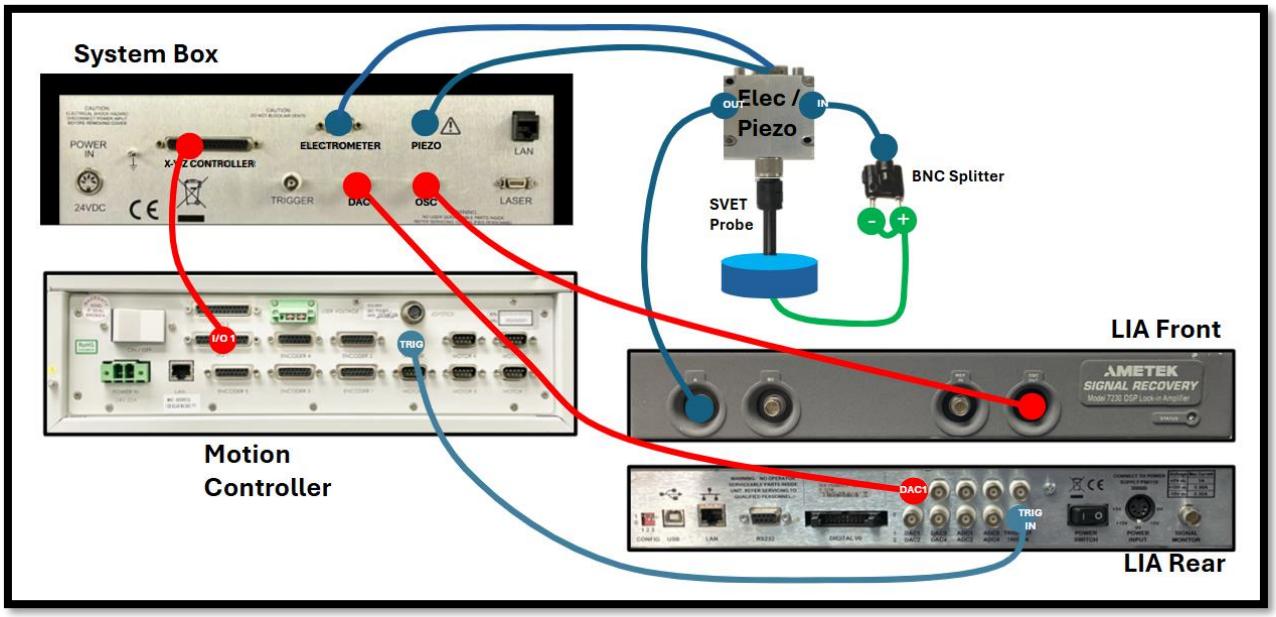


Figure 93. SVET Open Circuit Cable Connections

Cable Connections for a Galvanostatic/Potentiostatic controlled sample are below.

NOTE VersaSTAT 4A will be operated in floating mode with Versa Studio software. Grounded potentiostat (e.g., VersaSTAT 3 and VersaSTAT 4) and non-AMETEK potentiostats are applicable. Please contact Technical Support regarding the alternative instrument and cell connections.

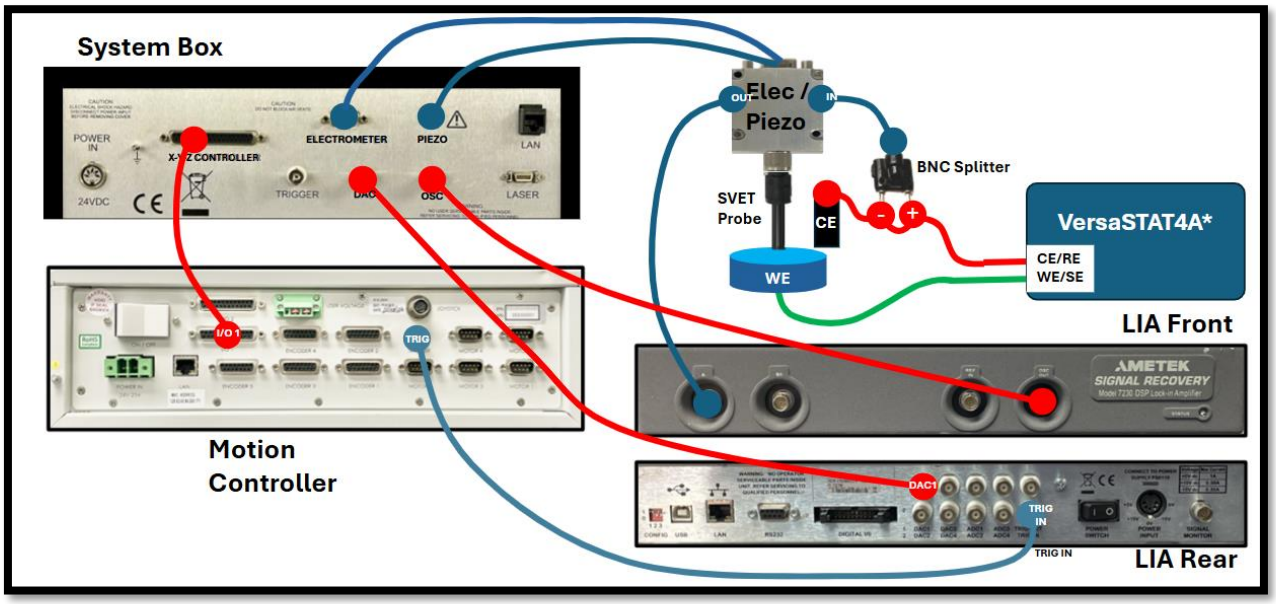


Figure 94. SVET Galvanostatic/Potentiostatic Controlled Sample Cable Connections

7.5 Software Control for VSC-SVET

7.5.1 Comments

Any comments that need to be stored with the data file can be entered into this field.

Please note that all the Scan and Measurement parameters from the experiments are already stored in each data file, so those are not necessary to be entered here.

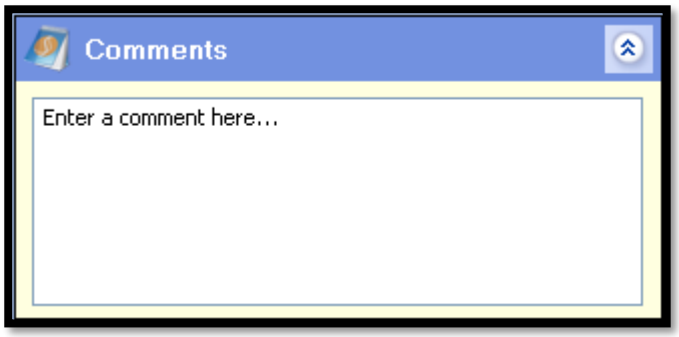


Figure 95. Software Comments Field

7.5.2 Conditioning

The Conditioning tab allows the user to set the time for the system to be delayed before any measurement in the Step is started. Note this programmed delay occurs once before the experiment starts. The Measurement & Delay window allows other specific delays between each line and between each point to be programmed. The units for the description of time are also selectable.



Figure 96. Software Conditioning Field

7.5.3 Scan Setup

Scan Setup is a generic tab that has a familiar look and feel in all the techniques.

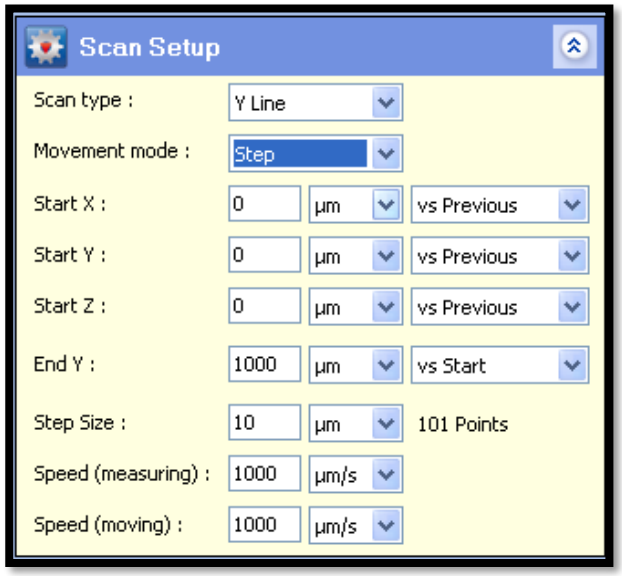


Figure 97. Scan Setup

7.5.3.1 Scan Type

The “Scan type” allows the user to define if the experiment is going to be executed in a single line axis or in an area as a series of line experiments. “X Line” would be a single line of data in X, while maintaining a constant Y and Z position. “Y-Line” scans in Y as “Z Line” scans in Z.

“XY Area” will map an Area in the XY plane. This is accomplished by a series of X scans at different Y positions. Data acquisition occurs as the probe moves from Start X to End X. (e.g., for -X to +X this is left to right).

“Point” will execute the experiment without moving the probe.

7.5.3.2 Measurement Mode

In this field, the user defines if the experiment is run in "Step" or "Sweep".

"STEP" will oversample and average the data. The probe moves to a given location and remains in that location for the measurement duration. Then, it moves stepwise to the new location (1 x Step Size; here 10 microns). Oversampled data collection again occurs at the new location. Data is averaged and reported. This oversampling and averaging process reduces the noise in the experiment but increases the duration of the experiment.

"SWEEP" will acquire data while the probe is moving. Data is not oversampled, which decreases the overall duration of the experiment, but may affect data quality. Time Constant of the signal chain should be considered when setting the Sweep parameters, as the probe's position is changing as data is coming from the signal chain.

7.5.3.3 Start X / Y / Z

In this field, the user defines the specific position that the experiment starts.

This can be set as "vs. Previous" or "vs. Absolute".

"vs. Previous" will allow the probe to use its current position as the origin point. In this example, 0/0/0 vs. Previous starts the experiment from the probe's current position.

"vs. Absolute" will use the known extreme position in order to keep an absolute reference grid from which positions are specified. 0/0/0 would be the far left (-X); back (-Y) and down (-Z).

7.5.3.4 End vs. Start

In this field, the user defines the location where the experiment is terminated.

The "Start" and "End" define the distance or area over which the experiment is performed.

The dimensions of the Scan Area should be considered when Aspect Ratio of the data of the end-result.

7.5.3.5 Step Size

This field defines the data point density. A data point is acquired and recorded at every Step size. High resolution experiments would require small step size as one component.

In Area Scan, the user can define different densities in X and Y. Pixels do not have to be squares (equal X and Y) but it is recommended and set as the default.

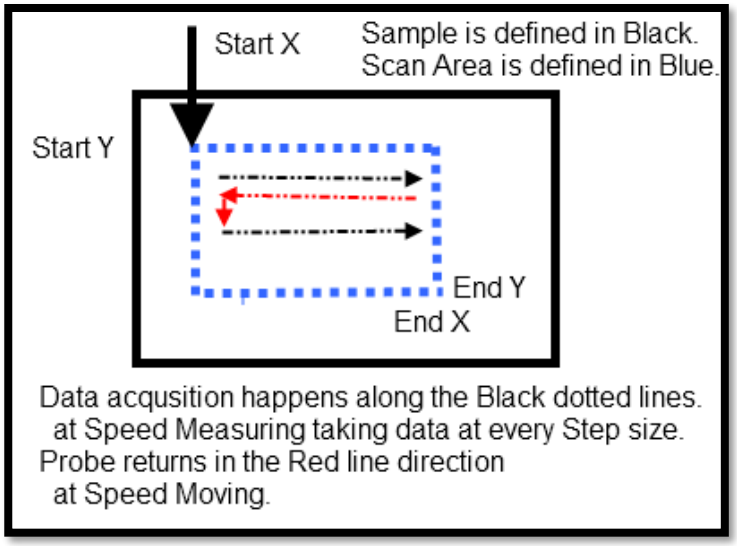


Figure 98. Area Scan

7.5.4 Signal Conditioning

In order to tune to Signal Conditioning most effectively, the probe should be positioned in X,Y over the most active region (highest signal).

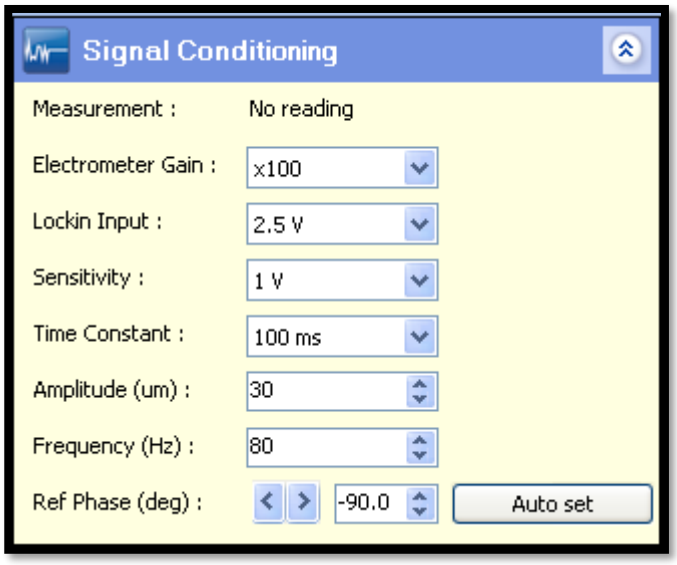


Figure 99. Software Signal Conditioning

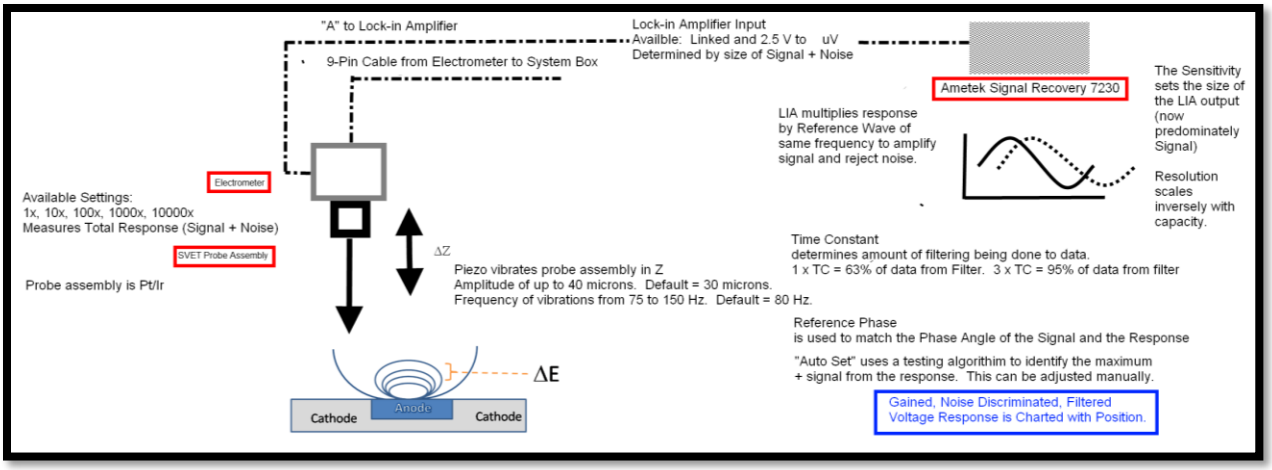


Figure 100.VSC-SVET Signal Conditioning Diagram

7.5.4.1 Electrometer Gain

The Electrometer measures the response of the probe. Gains are Selectable from 1x to 10,000x in decades. Gain is applied equally to the entire response; Signal + Noise.

Increasing the Gain will make small signals easier to measure; however, care must be given not to reach an Overload condition. A helpful Overload indicator provides information when the measurement is Overloaded. Users can then either reduce gain or increase sensitivity.

Consider:

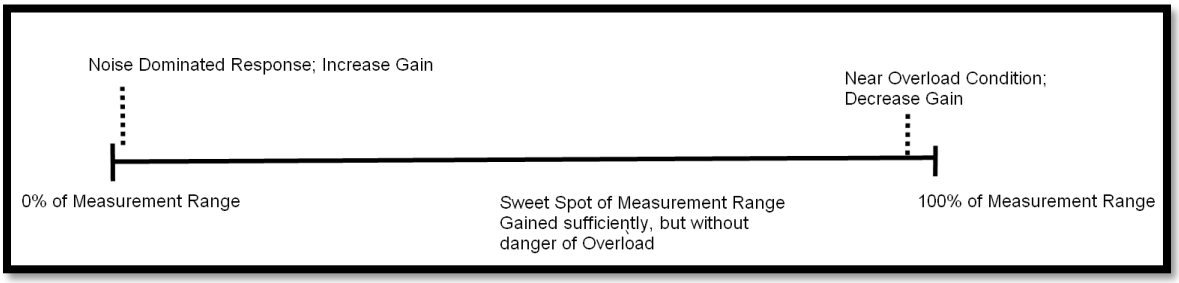


Figure 101. Electrometer Gain Diagram

The Electrometer is encased in a chromated aluminum housing.

7.5.5 The Lock-In Amplifier

Voltage is applied to the piezo unit from the System Box to drive the vibrations.

A Lock-in Amplifier measures an AC input and provides a DC output proportional to its magnitude. VersaSCAN uses a Signal Recovery Lock-in Amplifier 7230, but all Ethernet LIA from Signal Recovery are compatible.

7.5.5.1 Lock-in Input.

The Lock-In Input can be adjusted to a level with appropriate capacity (high enough) and resolution (low enough) for the gained response coming from the Electrometer.

The default setting for this value is “Linked”. This scales the Lock-In Input to response levels from the Electrometer.

7.5.5.2 Time Constant.

The Time Constant sets the amount of filtering on the data.

The longer the Time Constant, the more filtering is done.

The Time Constant should be matched to the amount of time the probe is in a given location and the difference in measured values of consecutive points.

The Signal Recovery Lock-in Amplifier uses a digital 12db finite impulse response (FIR) filter. The Output reaches 100% after 4 x TC.

For faster experiments, decrease the Time Constant settings in the Signal Conditioning window and watch the noise level in the Measurement.

7.5.5.3 Reference Wave

The LIA uses an internally generated Reference Wave at the characteristic frequency at which the piezo is vibrating.

The gained response from the Electrometer has both Signal and Noise components. Noise will appear randomly distributed across the frequency domain. Signal will appear at the characteristic measurement frequency of the probe (via the piezo).



Figure 102. SVET Reference Wave Signal

Users must be sure that the Reference Phase of the Reference Wave is coherent with the incoming Response. If it is 90 degrees out-of-phase, the output response goes to zero. If it is 180 degrees out-of-phase, it should have the same magnitude and opposite sign.

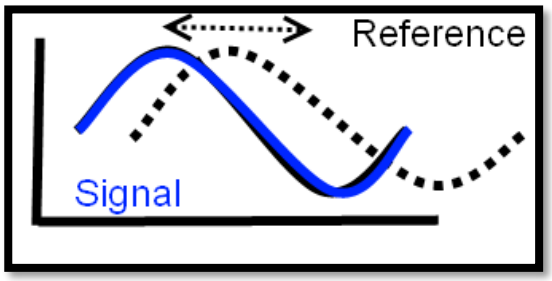


Figure 103. Reference Wave Diagram

Manual adjustment of the Reference Phase should follow an AC response.

This is a good additional check that the measured response is dominated by signal and not noise.



Figure 104. Software Reference Phase Settings

The Up and Down arrows will move the Reference Phase in 5-degree increments. Note the effect on the Measurement. The Left and Right arrows will quickly move the Reference Phase in 90-degree increments. Using the "Auto Set" will allow the Lock-in Amplifier to use its logic to determine the Reference Phase that gives the highest positive value. 180 degrees from that value will be the highest magnitude negative signal. This is a convenient tool to quickly lock on the highest signal and change its polarity if desired.

The Sensitivity is adjusted to handle the output of the Lock-in Amplifier, after the noise has been discriminated against.

The Amplitude setting determines the distance in Z over which the probe is vibrated. This range can be set from 0 microns to 40 microns with 30 microns being the default. The vibration amplitude should be considered when comparing results. The amplitude of vibration should scale with the voltage difference.

The Frequency of vibration is available for the user to set. Available values are 75 Hz to 150 Hz. This range lets users avoid known frequencies or harmonies of local environmental noise sources. Higher frequencies may discriminate more but can cause convection (stirring) of the solution.

7.5.5.4 Measurement and Delay

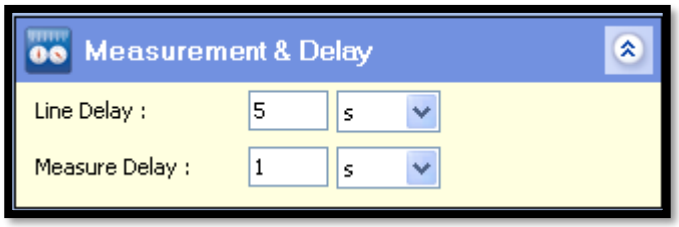


Figure 105. Measurement and Delay Settings

7.5.5.5 Line Delay

The Line Delay allows the user to program a set time delay between each line of data acquisition.

This is helpful when waiting for motion in the electrolyte (convection) caused by the return scan to settle. Additionally, highly filtered data (long Time Constants) can benefit from using this to allow the data to exit the filter.

7.5.5.6 Measure Delay

This mode is available in STEP mode only.

This complementary delay is at every point during the scan.

Conditioning: Delay at the start of the experiment.

Line Delay: Delay is at the start of each line.

Measure Delay: Delay is at each data point.

7.6 VSC-SVET System Test Procedure for Gold Wire Test Sample

This document assumes that the system has been assembled per instructions in the accompanying guides.

1. Mount the VersaSCAN Gold Wire Test Sample (P/N 224116) into the cell and level it.

NOTE Both the L-Cell and mL-Cell are compatible.

2. Fill the cell with suitable electrolyte. Drinking water with a typical conductivity of 150µS/cm is suitable for the test sample. It is recommended that users check the conductivity with a conductivity meter. The electrolyte level should be such that all the electrodes are immersed in the liquid.

3. Connect the SVET probe (P/N 224111) to the Electrometer (P/N 224077).

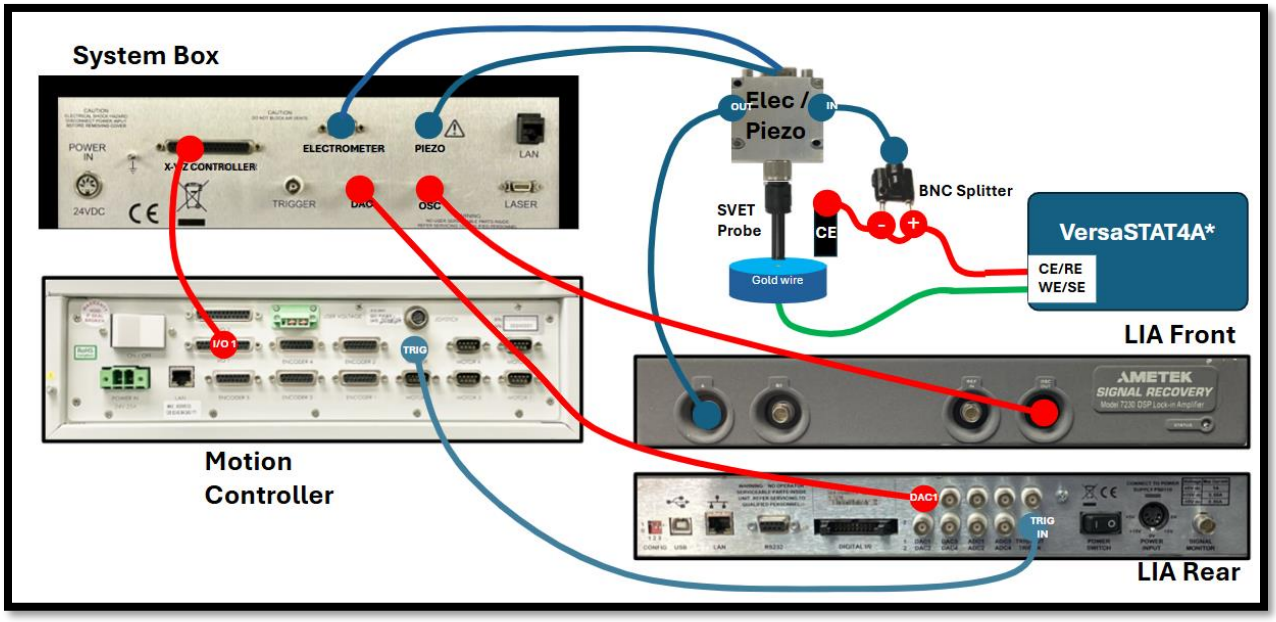


Figure 106. VSC SVET Setup for Gold Wire Test Sample

NOTE VersaSTAT 4A/3A/3F will be operated in floating mode with Versa Studio software. Grounded Potentiostat (e.g., VersaSTAT 3/4) and non-AMETEK are applicable with alternative cable connections. Please contact Technical Support for details.

4. Connect the Galvanostat to the electrodes in the cell.

5. Set the Galvanostat to generate a constant current of -10µA.

6. Use the Manual Control in the VersaSCAN software to position the tip of the SVET probe such that it is aligned above the gold wire of the test sample by approximately 100 micrometers. The Probe tip should be aligned precisely in the X&Y planes. Great care should be taken to avoid the tip of the probe from touching the sample. The probe tip is easily damaged by any contact. However, it should be noted that it is critical for successful operation of the technique that the probe to sample distance be as small as possible. This directly affects the spatial resolution of the technique, by virtue of geometry.

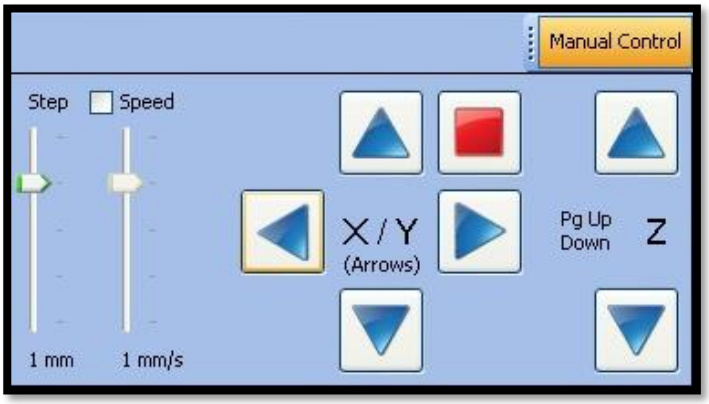


Figure 107. Manual Control Settings

7. In the VersaSCAN software select the menu option **File** and select **New Project**. Within the "Project" an Experiment is created. Insert a Step of the Scanning Vibrating Electrode Technique (SVET).

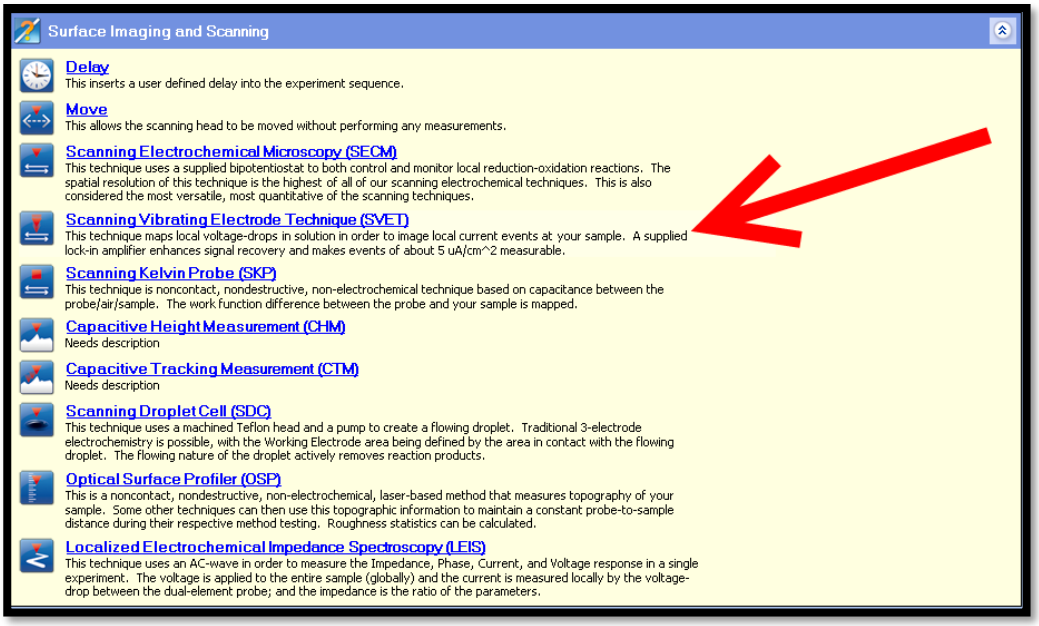


Figure 108. Surface Imaging and Scanning

The file Setup window for the SVET Step will be displayed. See VersaSCAN SVET Operator's Guide for a detailed explanation of all test parameters.

If the SVET probe is positioned directly over the gold wire, these parameters will cause a 4 mm x 3 mm area scan with the gold being centered.

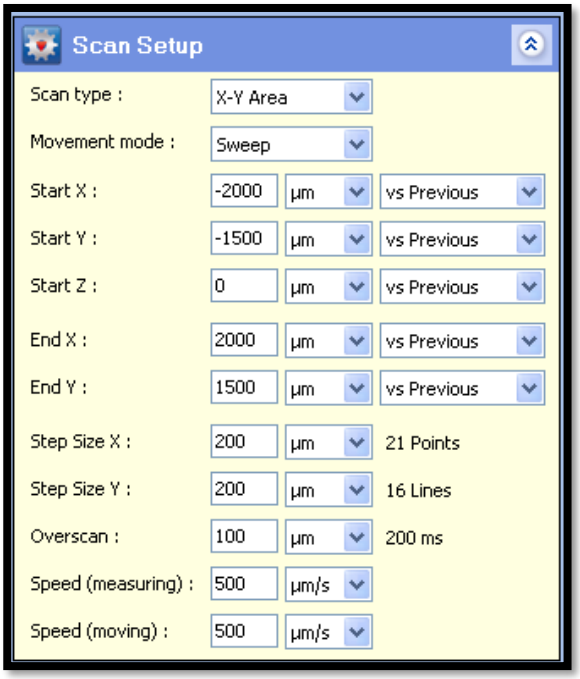


Figure 109. SVET Scan Setup

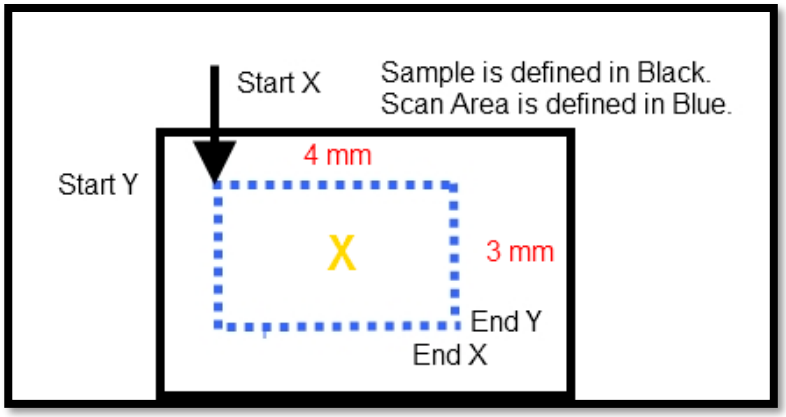


Figure 110. Scanning Area Diagram

8. The new experiment now needs to be configured. The SVET experiment Signal Configuration window will be displayed. See the VSC-SVET Users Guide for details on the controls.

   Since the SVET probe is positioned above the gold and the current is being applied, the maximum signal should be measured under the probe.

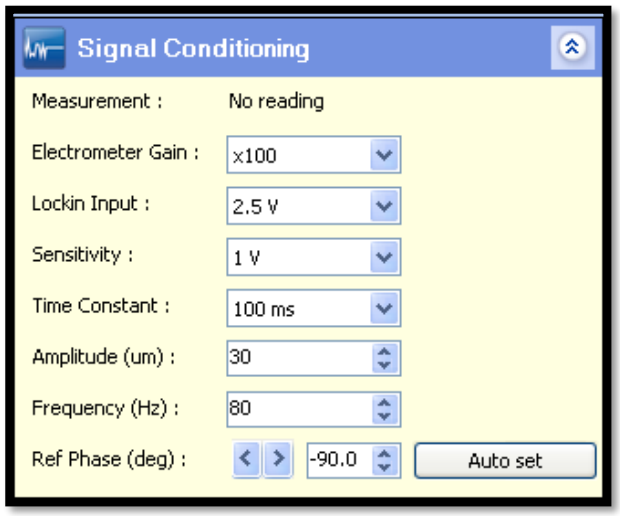


Figure 111. SVET Signal Conditioning

   Please note that the reference phase will need to be adjusted to the optimum value. The use of Auto will select a Reference Phase that gives the maximum positive signal.

9. Users should now be able to observe a signal in the output control of the "Measurement" window in terms of voltage. If the signal is low or non-existent, check the list below of possible reasons:

   - The Probe is not positioned directly over the XY center of the Gold Wire of the SVET Test sample.
   - The Probe to sample distance is too large. The optimum distance is 100µm.

- The cell connections are incorrect, and -10µA is not flowing through the PIS sample.
- The electrolyte is not covering all the electrodes.
- The electrolyte conductivity is not in the order of 150µS.
- The electrometer is overloaded.

10. Select **Run**. By starting the experiment with the suggested parameters, the probe will move -2 mm to the left and -1.5 mm in Y; then start at 4 x 3 mm experiment. Each line of the scan is completed, and the data is plotted on the line graph and on the area contour map.



Figure 112. Run Icon

11. The screenshot below shows the typical data obtained from the test experiment.

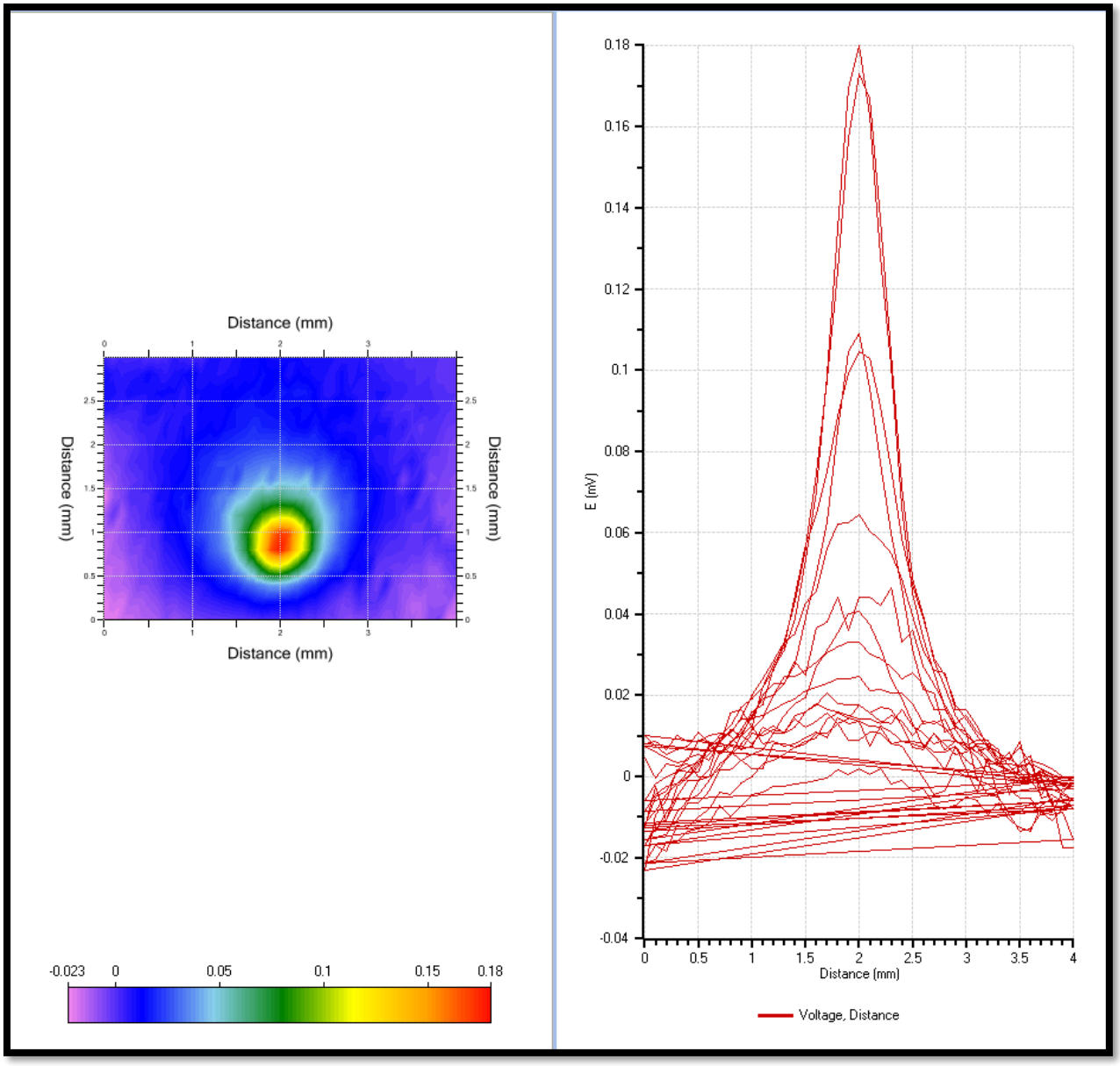


Figure 113. SVET Test Results

8. VERSASCAN SKP (VSC-SKP)

The VersaSCAN SKP is a Scanning Kelvin Probe (SKP). It requires VSC-BASE and VSC-SKP. It is recommended to use VSC-CAM and VSC-LCELL or VSC-mLCELL.

8.1 SVET Technique Overview and Introduction

The Scanning Kelvin Probe technique works on the principle of capacitor. The VSC-SKP uses a tungsten wire as its measurement element. As a metal, the probe material has electrons, and those electrons have a certain amount of inherent energy and thus an average energy level ("Fermi Level" to electrochemists). The difference between this average energy level and that of vacuum is one definition of work function. The work function is the energy (in eV or J) required to liberate an electron from the surface of a conductor.

Initially, the probe and sample are not connected, and they exist independent of each other. Then, in the initial phase of the experiment the probe and sample are "connected". This happens through the system. The probe and sample do not actually contact. Due to the difference in energy of the electrons of the sample and the probe, each develops a different polarity surface charge, and they balance through the electrical connection.

The probe/air/sample then forms a capacitor and some measurable value. The VSC-SKP applies a "nulling voltage" in order to "cancel" out that capacitance. The (nulling voltage) * -1 is then the difference in work function between the probe and the sample.

SKP experiments are often run in the absence of electrolyte and thus are considered physical or materials measurements rather than electrochemical ones. However, these can be correlated.

A piezo unit vibrates the probe in Z-direction (axis perpendicular to the sample). The amplitude of vibration may be only tens of microns peak-to-peak. This small vibration provides a very small voltage to be measured. Therefore, the response (signal + noise) at the probe is then amplified by the electrometer. The gained output of the electrometer is then input to a Lock-in Amplifier. This, in turn, uses a phase detector along with a Reference at the same frequency of vibration to extract the small AC signal from the entire measured response. The VersaSCAN capitalizes on Ametek's industry-leading Noise Characteristics of the Signal Recovery 7230 Lock-in Amplifier to provide superior measurement of these small signals. The voltage is recorded, and the probe is repositioned. A data map results as voltage versus position are displayed.

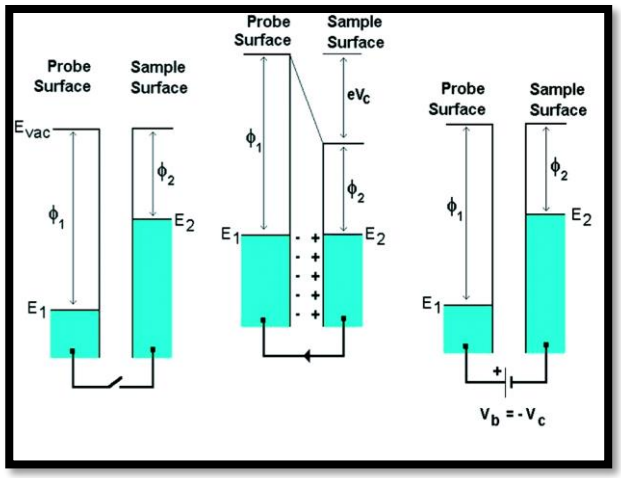


Figure 114. Energy Levels at Different Stages of the SKP Experiment

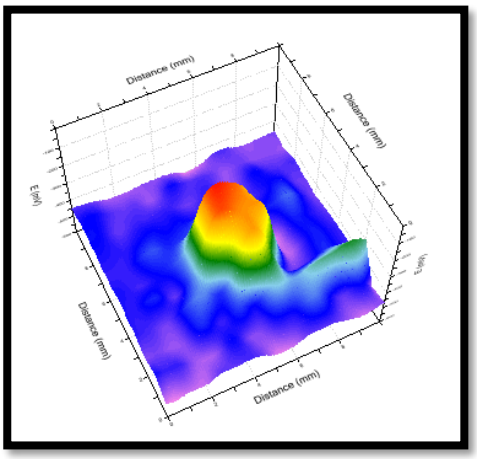


Figure 115. Zinc/Galvanized Steel Response Using VSC-SKP

8.2 Key Points of SKP

General statements about Scanning Kelvin Probe

- Non-destructive
- Non-contact
- Measures Work Function difference being probe and sample.
  This work function difference can be related to Ecorr by building a calibration curve.
- Typically measured in atmospheric conditions
- Measures over conducting surface, even with an insulation coating over it.

The VSC-SKP vibrates the probe and uses a supplied Signal Recovery Lock-In Amplifier for enhanced signal recovery.

- Can operate in "Topography Mode"
- Can then be used in Height-Tracking mechanisms
- Probe is either a 500-micron diameter tungsten wire in a brass sheath (P/N 224112) or a 250-micron diameter tungsten wire in a brass sheath (P/N 224113)

8.3 VSC-SKP Packing List

Table 14. VSC-SKP Packing List

Description	Ametek PN	Quantity (Each)
Potentiostats		
Dual Phase DSP Lock-in Amplifier	7230-VS	1
VersaSCAN System Control Box*	224118-PT	1
Piezo Motion Unit*	233737	1
SCR M3x0.5-14mm SHCS 316ss	233792	2
Electrometer		
VersaSCAN Electrometer*	224077	1
SHCS M3X0.5-25mm	233848	4
Probes and Electrodes		
VersaSCAN SKP Probe, 500 µm	224112	1
VersaSCAN SKP Probe, 250 µm	224133	1
Test Sample		
VersaSCAN SKP Test Sample	224117	1
Connectivity and Power Cables*		
Extension Cord	803937	2
Cable, 9-PIN M/M	233973	2
Cable, Data DB-9 M/M	233918	1
Cable, Data DB-25 – DB-37, M/F	1116426	1
Cable, Data DB37, M/M	1107199	1
Cable, BNC-BNC	SC0033	3
Cable, Trigger, SMA-BNC, 1m	1116486	1

*Indicates that item is used on multiple techniques and will not be duplicated in shipment.

8.4 Cable Connections for VSC-SKP

> **NOTE** If the system has TWO motion controller boxes, please refer to Appendix 1 for set-up diagrams.

The diagrams are additionally available as part of the “Setup” of each experiment.



Figure 116. SKP Setup Diagram

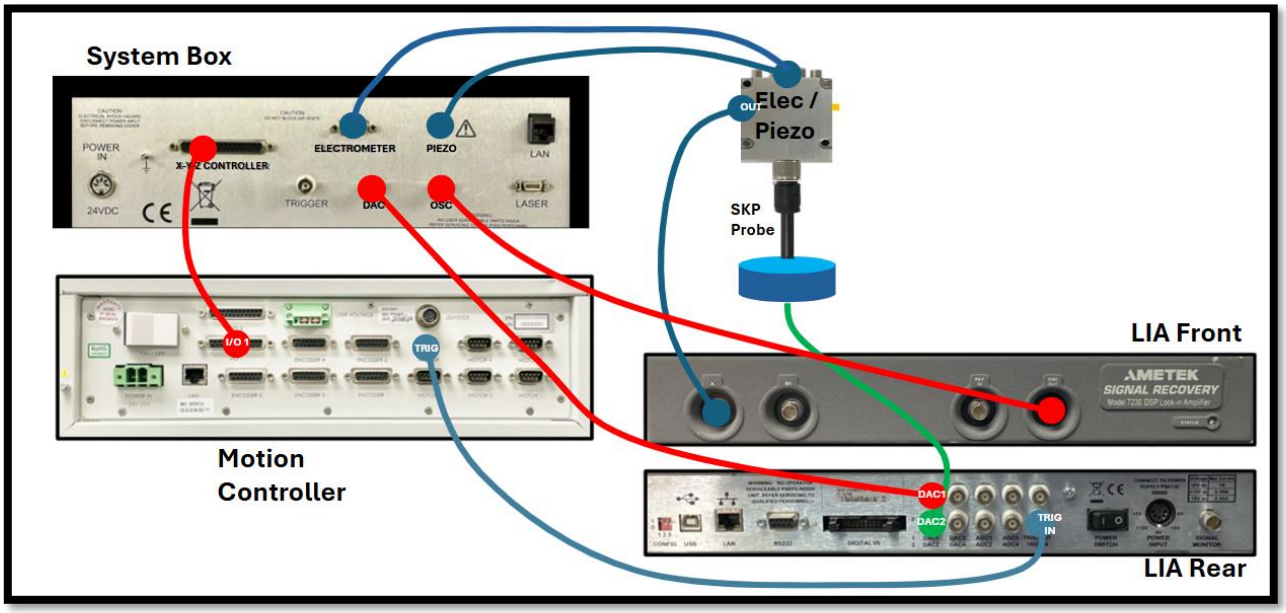


Figure 117. SKP Cable Connections

Table 15. Cell Connections for SKP

OUT	IN	CABLE
Motion Controller (XYZ)	System Box (XYZ)	25-PIN to 37-PIN and 37-PIN to 37-PIN
Top of Electrometer	System Box (Electrometer)	9-Pin Male to Male
Top of Piezo	System Box (Piezo)	Mount to Piezo
"A" on the front of the SR7230	Left Side of Electrometer ("A")	BNC-to-SMC
TRIG on the back of the SR7230	Trig on Motion Controller	BNC-to-SMA
DAC 1 on back of SR7230	System Box (DAC)	BNC-to-BNC
DAC 2 on back of SR7230	Sample	BNC-to-Alligator/Sample
OSC on front of SR7230	System Box (OSC)	BNC-to-BNC

8.5 Software Control for VSC-SKP

8.5.1 Comments

Any comments that need to be stored with the data file can be entered into this field.

Please note that all the Scan and Measurement parameters from the experiments are already stored in each data file, so those are not necessary to be entered here.

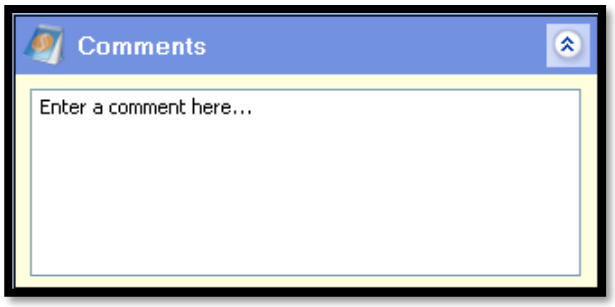


Figure 118. Software Comment Field

8.5.2 Conditioning

The Conditioning tab allows the user to set the time for the system to be delayed before any measurement in the Step is started. Note this programmed delay occurs once before the experiment starts. The Measurement & Delay window allows other specific delays between each line and between each point to be programmed. The units for the description of time are also selectable.



Figure 119. Conditioning Tab

8.5.3 Scan Setup

Scan Setup is a generic tab that has a familiar look and feel in all the techniques.

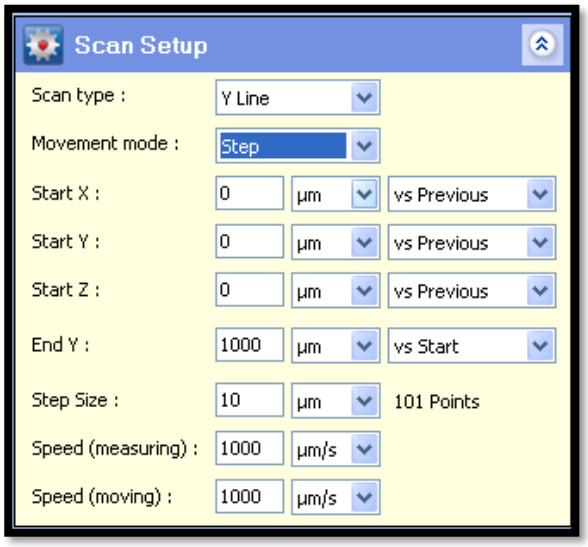


Figure 120. Software Scan Setup

8.5.3.1 Scan Type

The "Scan type" allows the user to define if the experiment is going to be executed in a single line axis or in an area as a series of line experiments. "X Line" would be a single line of data in X, while maintaining a constant Y and Z position. "Y-Line" scans in Y as "Z Line" scans in Z.

"XY Area" will map an Area in the XY plane. This is accomplished by a series of X scans at different Y positions. Data acquisition occurs as the probe moves from Start X to End X (e.g., for -X to +X this is left to right).

"Point" will execute the experiment without moving the probe.

8.5.3.2 Measurement Mode

In this field, the user defines if the experiment is run in "Step" or "Sweep".

"STEP" will oversample and average the data. The probe moves to a given location and remains in that location for the measurement duration. Then, it moves stepwise to the new location (1 x Step Size; here 10 microns). Oversampled data collection again occurs at the new location; data is averaged and reported. This oversampling and averaging process reduces the noise in the experiment but increases the duration of the experiment.

"SWEEP" will acquire data while the probe is moving. Data is not oversampled, which decreases the overall duration of the experiment, but may affect data quality. Time Constant of the signal chain should be considered when setting the Sweep parameters, as the probe's position is changing as data is coming from the signal chain.

8.5.3.3 Start X/Y/Z

In this field, the user defines the specific position that the experiment starts.

This can be set as "vs. Previous" or "vs. Absolute".

> "vs. Previous" will allow the probe to use its current position as the origin point. In this example, 0/0/0 vs. Previous starts the experiment from the probe's current position.
>
> "vs. Absolute" will use the known extreme position in order to keep an absolute reference grid from which positions are specified. 0/0/0 would be the far left (-X) ; back (-Y) and down (-Z).

8.5.3.4 End vs. Start

In this field, the user defines the location where the experiment is terminated.

The "Start" and "End" define the distance or area over which the experiment is performed.

The dimensions of the Scan Area should be considered when Aspect Ratio of the data of the end-result.

8.5.3.5 Step Size

This field defines the data point density. A data point is acquired and recorded at every Step size.

High resolution experiments would require small step size as one component.

In Area Scan, the user can define different densities in X and Y. Pixels do not have to be squares (equal X and Y) but it is recommended and set as the default.

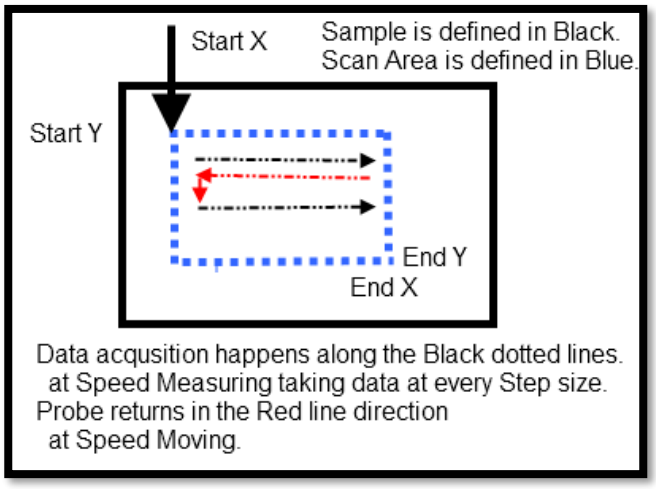


Figure 121. Area Scan

8.5.4 Signal Conditioning

In order to tune to Signal Conditioning most effectively, the probe should be positioned in X,Y over the most active region (highest signal).

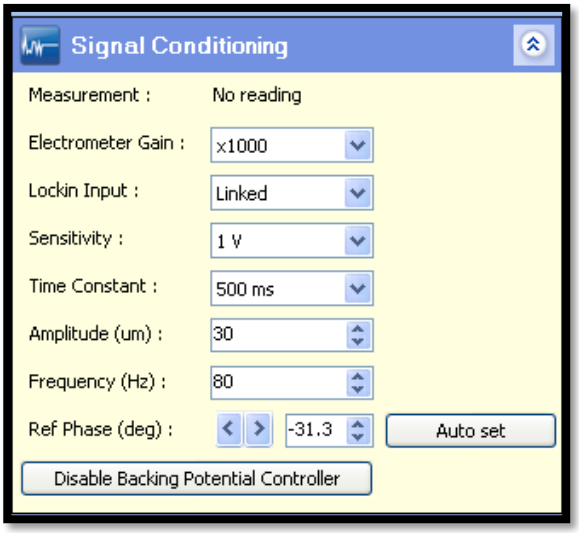


Figure 122. Signal Conditioning

8.5.5 Backing Potential Controller

The Backing Potential Controller (BPC) is the electronics that applies the nulling voltage to the sample. This is accessed through DAC2 on the back of the SR 7230 Lock-in Amplifier.

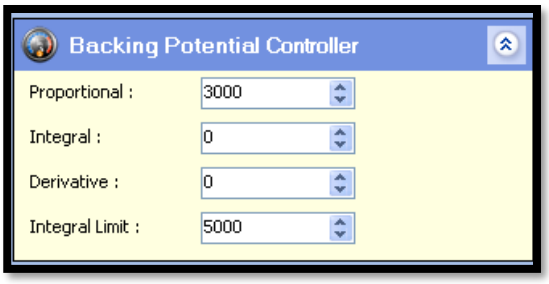


Figure 123. Backing Potential Controller

The Backing Potential Controller uses Proportional Integral Derivative (PID) logic to make these determinations. The applied voltage is tweaked, and the response is charted, then PID protocol is used to make continually more intelligent decisions to arrive incrementally closer to the correct nulling voltage.

Description of these different PID parameters is beyond the scope of this document, but detailed descriptions are commonly available in the public domain.

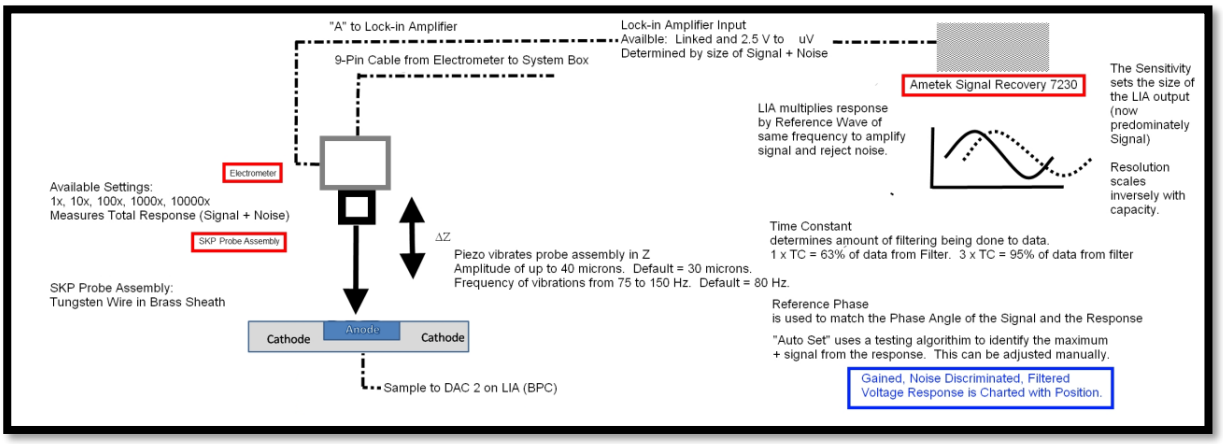


Figure 124. VSC-SKP Signal Conditioning Diagram

8.5.6 Electrometer Gain

The Electrometer measures the response of the probe. Gains are Selectable from 1x to 10,000x in decades. Gain is applied equally to the entire response; Signal + Noise.

Increasing the Gain will make small signals easier to measure; however, care must be given not to reach an Overload condition. A helpful Overload indicator provides information when the measurement is Overloaded. Users can then either reduce gain or increase sensitivity.

Consider:

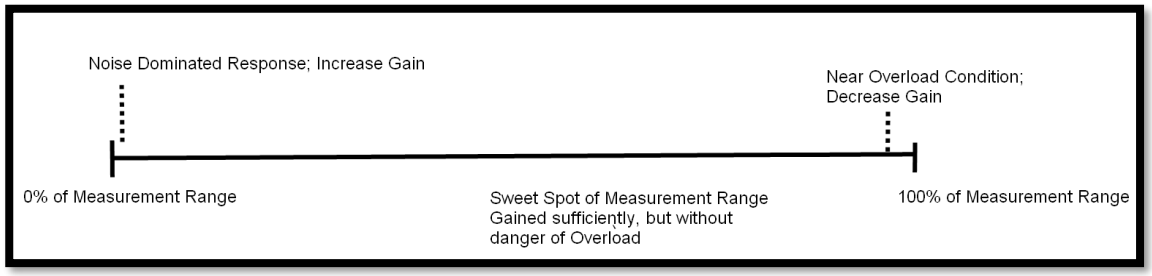


Figure 125. Electrometer Gain Diagram

The Electrometer is encased in a chromated aluminum housing.

8.6 The Lock-In Amplifier

Voltage is applied to the piezo unit from the System Box to drive the vibrations.

A Lock-In Amplifier measures an AC input and provides a DC output proportional to its magnitude. VersaSCAN uses a Signal Recovery Lock-in Amplifier 7230, but all Ethernet LIA from Signal Recovery are compatible.

8.6.1 Lock-In Input

The Lock-In Input can be adjusted to a level with appropriate capacity (high enough) and resolution (low enough) for the gained response coming from the Electrometer.

The default setting for this value is “Linked”. This scales the Lock-In Input to response levels from the Electrometer.

8.6.2 Time Constant

The Time Constant sets the amount of filtering on the data.

The longer the Time Constant, the more filtering is done.

The Time Constant should be matched to the amount of time the probe is in a given location and the difference in measured values of consecutive points.

> The Signal Recovery Lock-in Amplifier uses a digital 12db finite impulse response (FIR) filter. The Output reaches 100% after 4 x TC.

For faster experiments, decrease the Time Constant settings in the Signal Conditioning window and watch the noise level in the Measurement.

8.6.3 Reference Wave

The LIA uses an internally generated Reference Wave at the characteristic frequency at which the piezo is vibrating.

The gained response from the Electrometer has both Signal and Noise components. Noise will appear randomly distributed across the frequency domain. Signal will appear at the characteristic measurement frequency of the probe (via the piezo).

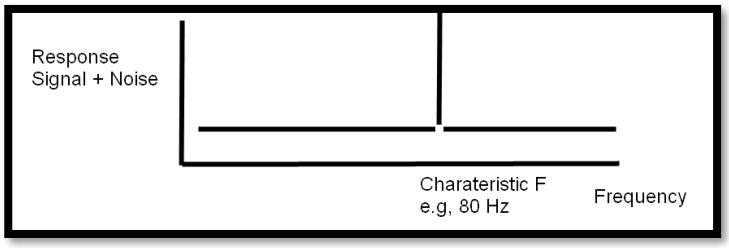


Figure 126. SKP Reference Wave Signal

Users must be sure that the Reference Phase of the Reference Wave is coherent with the incoming Response. If it is 90 degrees out-of-phase, the output response goes to zero. If it is 180 degrees out-of-phase, it should have the same magnitude and opposite sign.

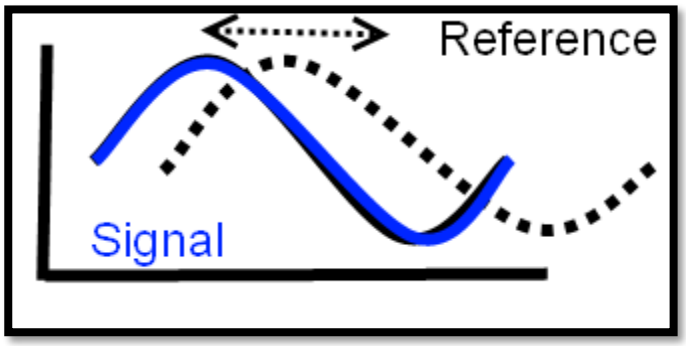


Figure 127. Reference Wave Diagram

Manual adjustment of the Reference Phase should follow an AC response.

This is a good additional check that the measured response is dominated by signal and not noise.



Figure 128. Software Reference Phase Settings

The Up and Down arrows will move the Reference Phase in 5-degree increments. Note the effect on the Measurement. The Left and Right arrows will quickly move the Reference Phase in 90-degree increments. Using the "Auto Set" will allow the Lock-in Amplifier to use its logic to determine the Reference Phase that gives the highest positive value. 180 degrees from that value will be the highest magnitude negative signal. This is a convenient tool to quickly lock on the highest signal and change its polarity if desired.

8.6.3.1 Sensitivity

The Sensitivity is adjusted to handle the output of the Lock-in Amplifier, after the noise has been discriminated against.

The Amplitude setting determines the distance in Z over which the probe is vibrated. This range can be set from 0 microns to 40 microns with 30 microns being the default. The vibration amplitude should be considered when comparing results. The amplitude of vibration should scale with the voltage difference.

The Frequency of vibration is available for the user to set. Available values are 75 Hz to 150 Hz. This range lets users avoid known frequencies or harmonics of local environmental noise sources. Higher frequencies may discriminate more but can cause convection (stirring) of the solution.

8.6.4 Measurement & Delay



Figure 129. Measurement and Delay

8.6.4.1 Line Delay

The Line Delay allows the user to program a set time delay between each line of data acquisition.

This is helpful when waiting for motion in the electrolyte (convection) caused by the return scan to settle. Additionally, highly filtered data (long Time Constants) can benefit from using this to allow the data to exit the filter.

8.6.4.2 Measure Delay

This mode is available in STEP mode only.
This complementary delay is at every point during the scan.

Conditioning: Delay at the start of the experiment

Line Delay: Delay is at the start of each line

Measure Delay: Delay is at each data point

8.7 VSC-SKP System Test Procedure for Zinc/Steel Sample

This document assumes that the VSC-BASE has been assembled per instructions in the accompanying guides.

The SKP test sample consists of a galvanized mild steel disk mounted on an epoxy holder. In the center of the sample a small area of the zinc has been etched away to expose the steel. The zinc and mild steel have different work functions which can be observed with the SKP technique. A connection wire is soldered to the underside of the metal.

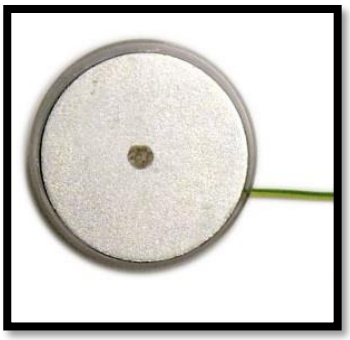


Figure 130. The SKP Test Sample

NOTE In Figure 130, the image shown is a test sample and not a reference sample.

Before running the SKP test sample experiment the sample must be mounted and leveled correctly in the cell (Recommend P/N VSC-LCELL). The sample must be electrically connected to the "DAC 2" port on the Lock-in Amplifier. This is the Backing Potential Controller.

The Piezo (P/N 233737) is mounted to the VersaSCAN Mounting Block (P/N 224061). The Electrometer (P/N 224077) is mounted directly to the Piezo. The SKP probe (P/N 224112 or 224113) is connected to the electrometer.

Table 16. SKP Cable Connections

OUT	IN	CABLE
Motion Controller (XY)	System Box (XY)	25-Pin to 25-Pin
Motion Controller (Z)	System Box (Z)	25-Pin to 25-Pin
Top of Electrometer	System Box (Electrometer)	9-Pin Male to Male
Top of Piezo	System Box (Piezo)	Mounted to Piezo
"A" on the front of the SR 7230	Left Side of Electrometer ("A")	BNC-to-SMC
TRIG on the back of the SR7230	Trig on Motion Controller	BNC-to-SMA
DAC 1 on back of SR 7230	System Box (DAC)	BNC-to-BNC
DAC 2 on back of SR 7230	Sample	BNC-to-Alligator/Sample
OSC on front of SR 7230	System Box (OSC)	BNC-to-BNC

The following steps should be taken to run the test sample:

1. Optionally remove the glass tank (P/N 224037) from the VSC-LCELL.

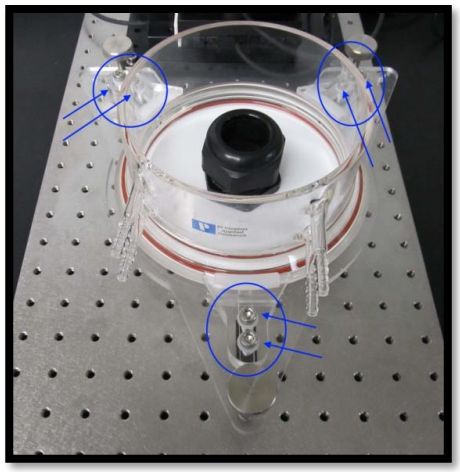


Figure 131. VSC-LCELL

2. Mount the SKP test sample into the cell and level it.

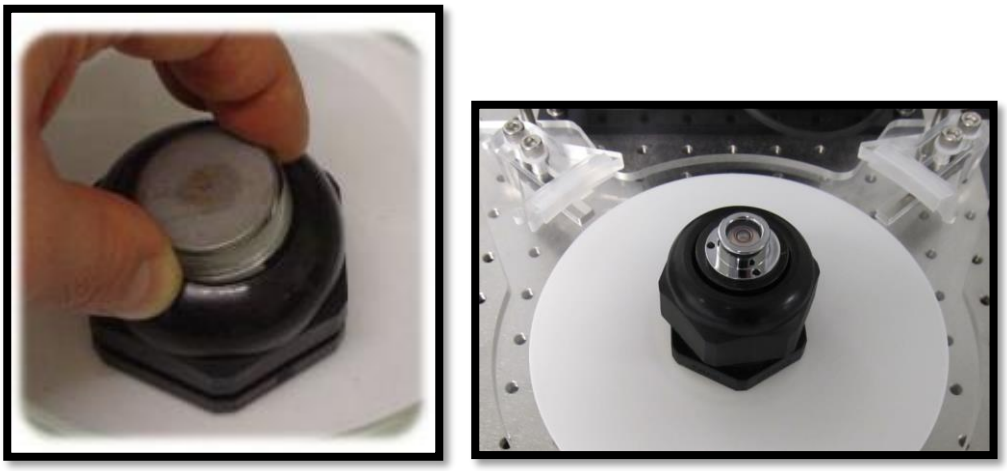


Figure 132. SKP Test Sample Mounted to Cell

3. Ensure all cabling is in place.

4. Position the axes in the extreme +Z to provide the most clearance for the SKP probe. Mount the SKP probe into the electrometer. Hold the body with one hand as the body is rotated until the keyed connector matches and the probe seats into the electrometer. Using the other hand (continue to hold the body of the probe), screw the connector into the mating electrometer connector. Note users should feel this grip. Carefully remove both hands from the probe and ensure it is well seated and not cross-threaded.

5. Use the Manual Stage in the VersaSCAN software to position the tip of the SKP probe such that it is aligned above the center of the test sample, in the center of the etched area. The probe tip to sample distance should be approximately 100 micrometers. The Probe tip should be aligned precisely in the X&Y planes. Great care should be taken to avoid the tip of the probe from touching the sample. The probe tip is easily damaged by any contact. However, it should be noted that it is critical for successful operation of the technique that the probe to sample distance be as small as possible. This directly affects the spatial resolution of the

technique, by virtue of geometry. As the probe gets closer to the sample surface, incrementally reduce the Step and Speed settings on the Manual Control.

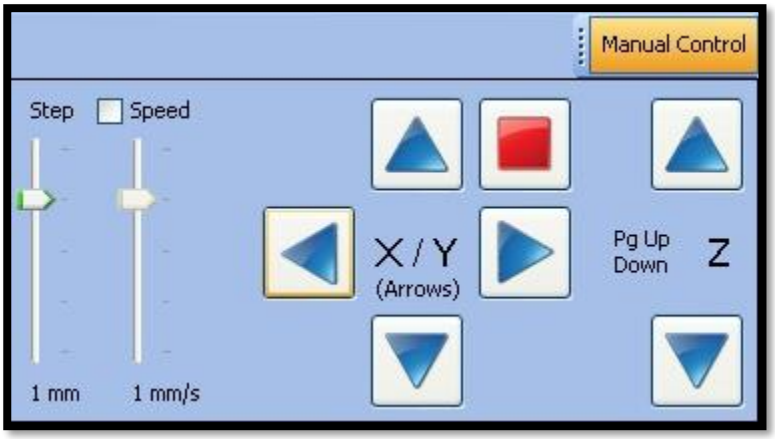


Figure 133. Manual Control Settings

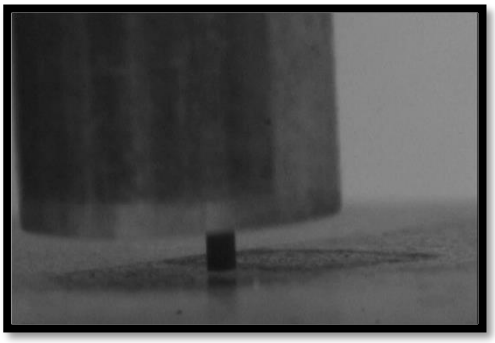


Figure 134. 500um SKP Probe @ 100 Microns from the Sample

NOTE In Figure 134, the reflection of the probe is an estimation of Z. The image was taken using optional VSC-CAM.

6. In the VersaSCAN software select the menu option **File** and select **New Project**. Within the "Project" an Experiment is created; Insert a Step of the Scanning Kelvin Probe (SKP).

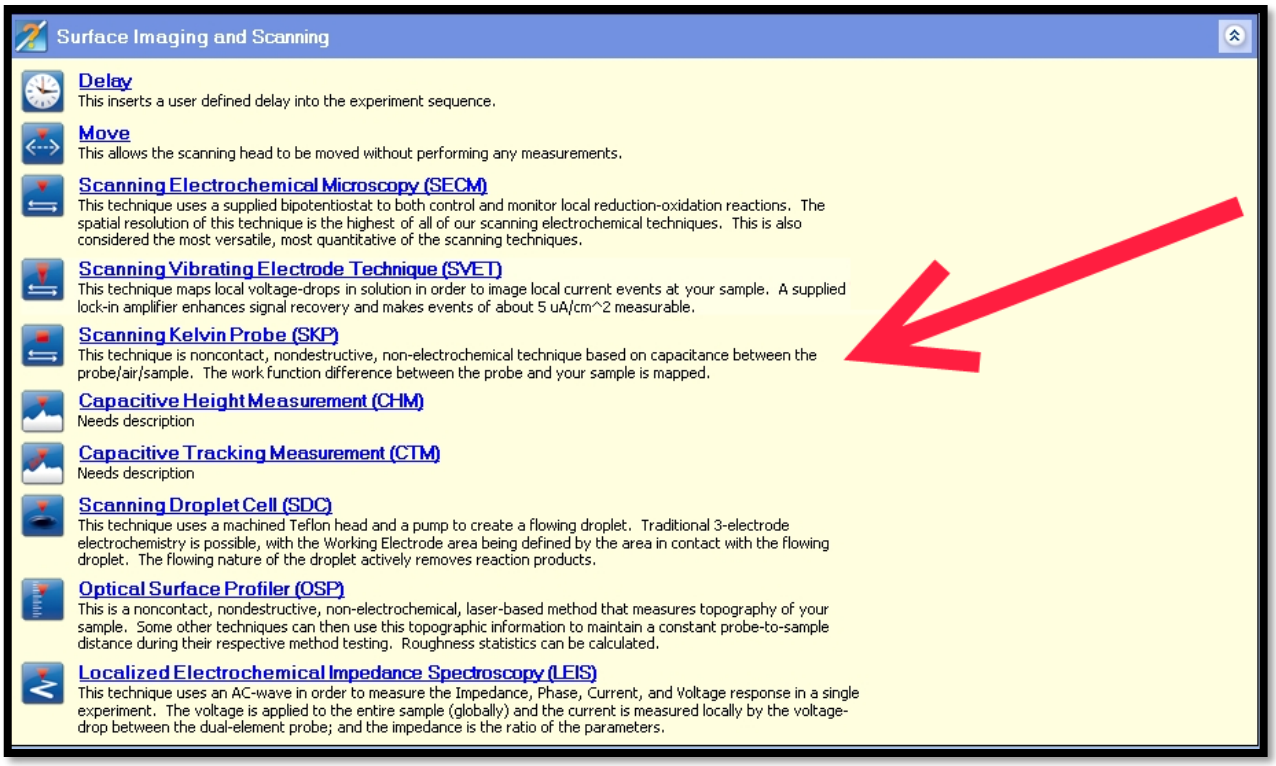


Figure 135. Surface Imaging and Scanning

The file Setup window for the SKP Step will be displayed. See VersaSCAN Operator's Guide to detailed explanation of all test parameters.

7. If the SKP probe is positioned directly over the etched area on the SKP Test Sample, these parameters will cause a 10 mm x 10 mm area scan with the etched area centered.

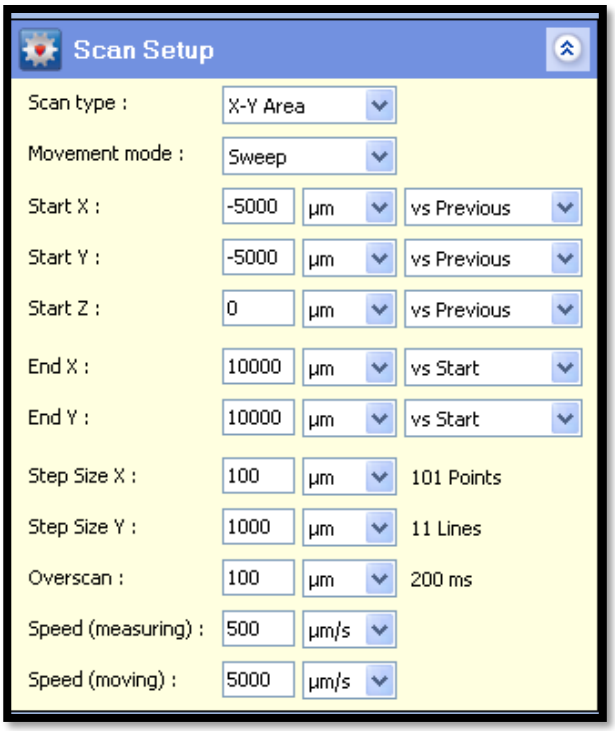


Figure 136. SKP Scan Setup

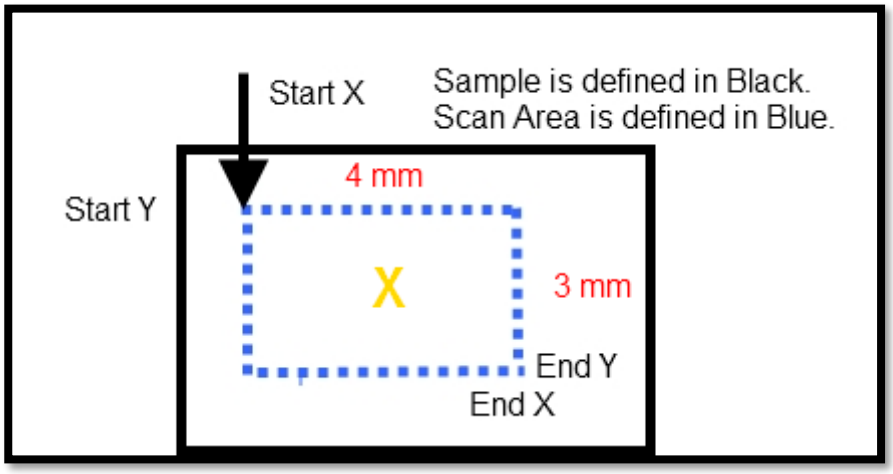


Figure 137. SKP Scan Area

The new experiment now needs to be configured. The SKP experiment Signal Configuration window will be displayed. See the VSC-SKP Users Guide for details on the controls.

8. Since the SKP probe is positioned above the etched area, the maximum signal should be measured under the probe.

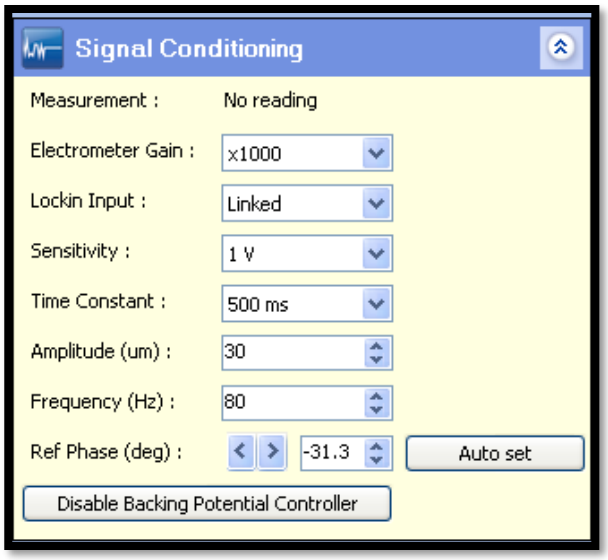


Figure 138. SKP Signal Conditioning

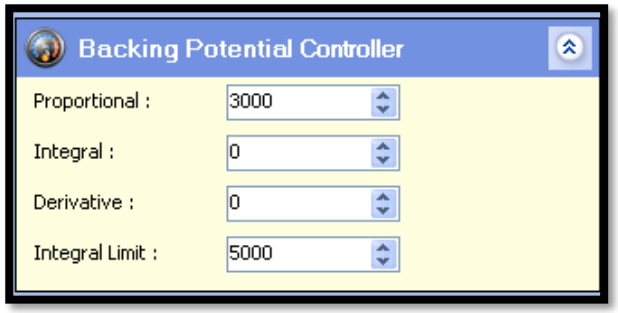


Figure 139. Backing Potential Controller

Please note that the reference phase will need to be adjusted to the optimum value. The use of Auto will select a Reference Phase that gives the maximum positive signal.

9. Users should now be able to observe a signal in the output control of the “Measurement” window in terms of voltage. If the signal is low or non-existent, check the list below of possible reasons:

    a. The Probe is not positioned directly over the XY center of the etched area of the SKP Test sample.
    b. The Probe to sample distance is too large. The optimum distance is 100µm.
    c. The cell connections are incorrect.
    d. The electrometer is overloaded.

10. Select **Run**. By starting the experiment with the suggested parameters, the probe will move -5 mm to the left and -5 mm in Y; then start at 10 x 10 mm experiment. Each line of the scan is completed, and the data is plotted on the line graph and on the area contour map.



Figure 140. Run Icon

11. The screenshot below shows the typical data obtained from the test experiment.

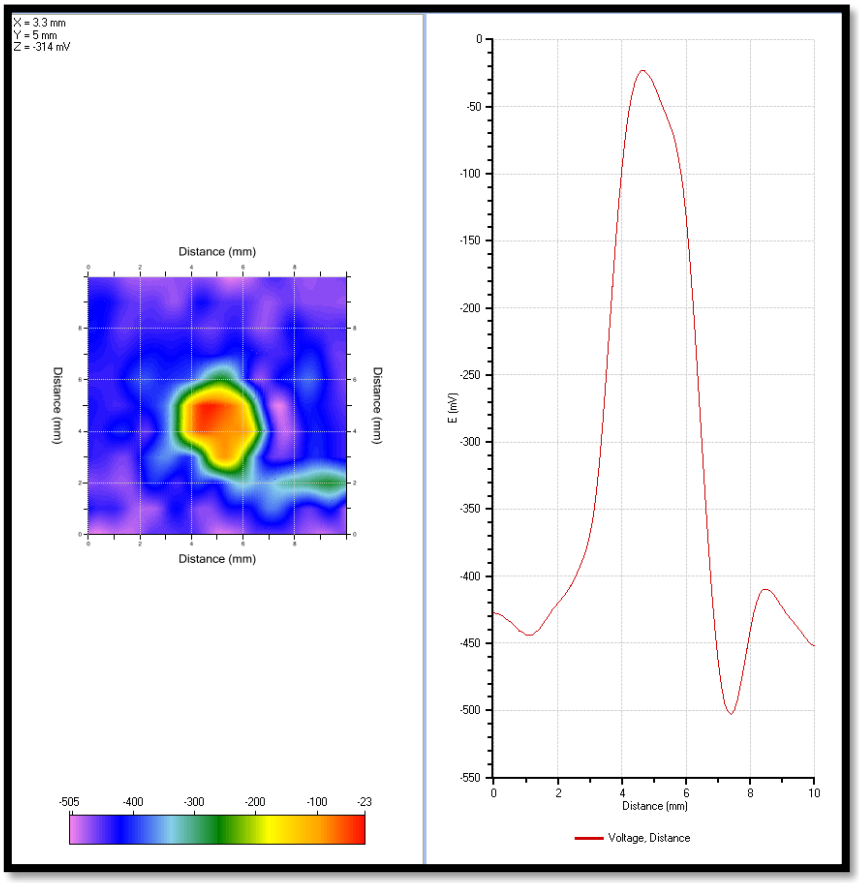


Figure 141. SKP Test Results

Please note that the SKP measurement is a relative measurement between the Probe work function and the surface work function, absolute values cannot be measured with this technique. The Surface Work function of both the probe and sample is variable; users should not expect to measure the same amplitude values each time they run the same sample. It may be useful to employ a reference sample. In corrosion measurement a copper cup containing copper sulfate solution is often used as a reference.

9. VERSASCAN SDC (VSC-SDC)

The VersaSCAN SDC is a Scanning Droplet Cell (SDC). It requires VSC-BASE and VSC-SDC. It is recommended to use VSC-CAM and VSC-LCELL.

9.1 SDC Technique Overview and Introduction

The Scanning Droplet Cell (SDC) is a technique of the VersaSCAN Scanning Electrochemical Workstation.

The SDC uses the positioning system to place the machined PTFE head in close proximity to the sample surface. A supplied peristaltic pump flows electrolyte from an external reservoir into this head. Once inside the head, the electrolyte flows past a Reference Electrode, out of the aperture, making a droplet with the surface of the sample, then past a Counter Electrode and into another reservoir. The wetted area is approximately determined by the capillary's inner diameter. A standard three-electrode electrochemical cell is created where the Working Electrode's electrochemical area is defined by the electrode // electrolyte interface, here being the droplet.

There are three variables that the experimentalists have in their toolboxes to study samples: position, applied electrochemical signal, flow-rate of the electrolyte. Each of these parameters can be set to study the effect on local response.

Spatial resolution is gained as the droplet is moved in X and/or Y created lines or area maps of data. Here constant signals – DC voltage, DC current, or open circuit – are applied, as position is the changing (independent) variable.

Constant or Dynamic signals can be applied if the head is kept stationary.

The droplet may be actively flowing to remove any reaction product from the sample surface, resulting in a constantly refreshed solution during the experiment or kept static to minimize flow at the surface. Flowrates are set by adjusting pump speed.

9.2 Applications

SDC can benefit any application of electrochemistry when a small subset of a sample needs to be investigated without cutting the larger sample. Corrosion and Physical Electrochemistry are two applications where most current research is being conducted with SDC.

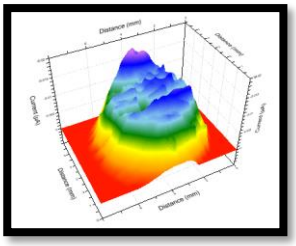


Figure 142. Results from Gold Disk in 3M KCl with -500 mV

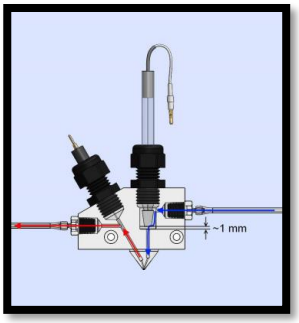


Figure 143. Schematic of the SDC Head with Reference and Counter Electrodes Installed

9.3 VSC-SDC Packing List

Table 17. VSC-SDC Packing List

Description	Ametek PN	Quantity (Each)
Potentiostats		
VersaSTAT 4A*	VersaSTAT 4A-400VS	1
Cable, VersaSTAT3 Cell, Optional	224065	1
Clip, Alligator, Fang, Barrel, Steel	233868	2
Pump and Tubing		
4 Channel Pump	233738	1
Tubing, 2-stop, PVC, 1.02mm ID, 900mm LG	233943	12
Beaker, Polypro, 100ml	233936	2
Tubing clamp, keck ramp clamp, 4.5mm	233935	2
Spacer		
VersaSCAN SDC Spacer	224142	1
SCR M3x0.5-14mm	233848	2
SDC Head and Mounting Hardware		
VersaSCAN SDC Head	224039	1
Electrode Adapter M12x1.5, .12-.26"	233933	2
O-ring, .39" ID, .06"WID, Buna-N	233934	2
Adapter, 1/16 NPT to 1/16 Tube ID	233767	3
Scr M3x0.5-14mm	233792	2
Electrodes		
Reference Electrode, AG/AGCL	K0265	3
Counter Electrode, PT Wire	233917	1
Control Box Bypass		
Cable, Adapter, VersaSCAN Sys Box	224145	1
Test Sample		
VersaSCAN Gold Disk Test Sample	224115	1
Connectivity and Power Cables*		
Extension Cord	803937	2
Cable, BNC-BNC	SC0033	1
Cable, Trigger, SMA-BNC, 1m	1116486	1

*Indicates that item is used on multiple techniques and will not be duplicated in shipment.

9.4 Cable Connections for VSC-SDC

> **NOTE** If the system has TWO motion controller boxes, please refer to Appendix 1 for set-up diagrams.

The diagrams are additionally available as part of the “Setup” of each experiment.

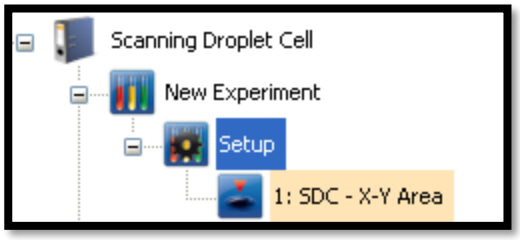


Figure 144. SDC Setup Diagram

Cable Connections for an Open Circuit controlled sample are below.

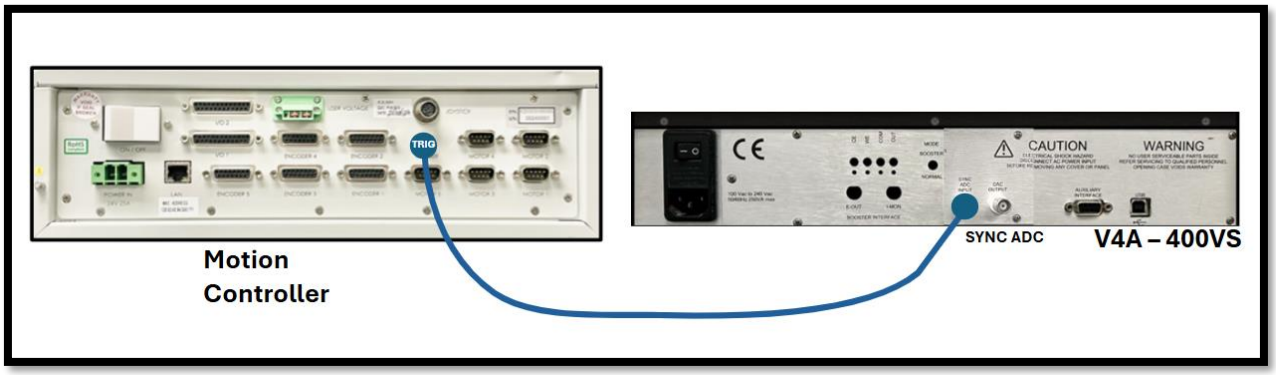


Figure 145. SDC Cable Connections

9.5 Preparing the VSC-SDC Head for Use

The VSC-SDC as shipped will have the Counter Electrode installed.

The Reference Electrode is shipped separately and must be installed.

Below are complete instructions for the installation in case parts must be cleaned during typical use or replaced due to wear.

Place the PTFE SDC Head in a bath of clean deionized water and ultrasonically clean the head for 10-15 minutes prior to use if the SDC Head has been used previously. This will help to dissolve any deposits that may have formed during previous experiments or will remove any dried salts if the SDC Head was not thoroughly and properly flushed with deionized water after its last use.

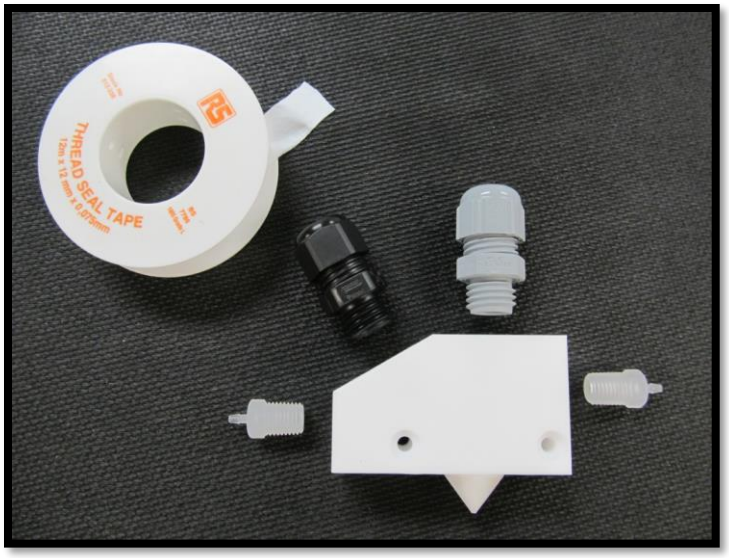


Figure 146. Parts Required for Preliminary/SDC Head Assembly

Apply PTFE Tape to seal the threads on the Cord Grips and Bayonet Hose Connectors against air leaks. See the example in the photo series below.

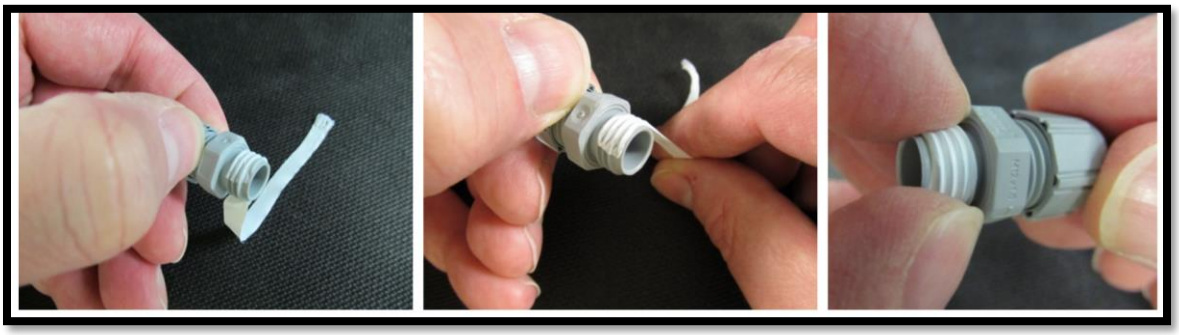


Figure 147. Placing the PTFE Tape

From left to right in the image above, start the PTFE tape such that it wraps around the fitting in a clockwise direction. Pull it slightly taught and wrap around the threads until two full revolutions have been completed and then cut (do not tear the tape) and smooth.

Repeat this process for the two miniature Bayonet Hose Connectors and the other Cord Grip. It is important to ensure the solution's flow is not obstructed with PTFE tape over the fittings' openings, but equally important that there is no route for air to enter the SDC head except for at the tip.

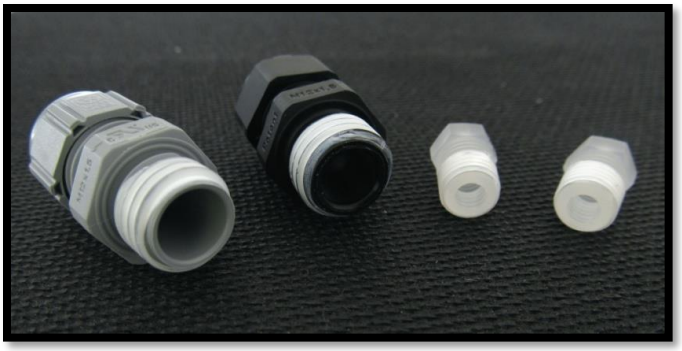


Figure 148. Fittings with PTFE Tape

When all fittings have PTFE tape on them, they should look similar to the above. Ensure that the bottom of the fittings and the openings are not obstructed with PTFE tape.

Thread all of the fittings into their respective openings in the SDC Head as shown in the photo below.

Use caution that the fittings are not forced into their openings. They should thread easily. If they do not, immediately STOP so as not to risk stripping/damaging the threads in the SDC Head. Remove the fitting and try again while ensuring the threads are properly aligned. The fittings should only be tightened by hand. No tools should be used to install the fittings.

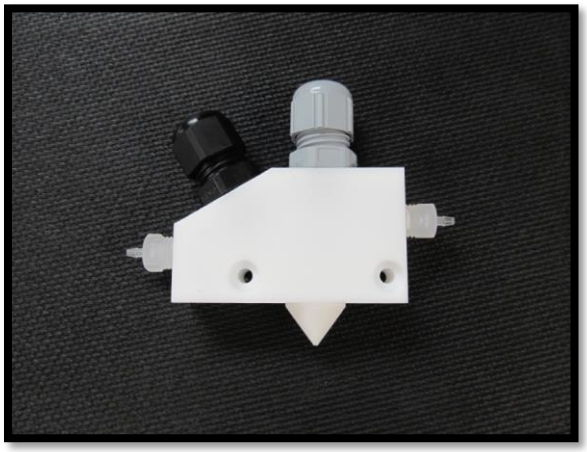


Figure 149. SDC Head with its Fittings Properly Installed

NOTE The Bayonet Hose Connectors will not thread completely into the SDC Head. Simply ensure that they are threaded in tightly by hand.

Prepare to install the Reference Electrode (see Reference Electrode Setup Section if working with a new electrode for its preparation prior to installation into the SDC Head) and Counter Electrode by removing only the Cord Grip caps as shown in the photo below.

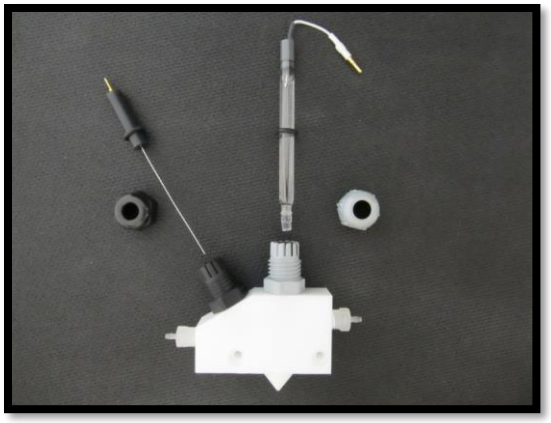


Figure 150. Cord Grip with Caps Removed

> **NOTE** The Counter Electrode mounts into opening on the left, angled portion of SDC while the Reference Electrode mounts into the opening on the right on the flat portion of SDC head.

Take care when inserting the Counter Electrode to ensure that its wire inserts into the opening in the center. Avoid bending the Counter Electrode's wire or running the wire into the PTFE body of the SDC Head. The latter can dislodge small pieces of PTFE debris that could block the capillary.



Figure 151. Looking into Counter Electrode Opening on SDC Head

Insert the Reference Electrode into the body of the SDC head as indicated in the picture below. Gently insert the Reference Electrode into the SDC head to the point where it stops on the internal seat, and then remove the Reference Electrode by ~ 1 mm. This ensures that the Reference Electrode is correctly positioned into the SDC Head for proper contact with the solution while ensuring the solution can flow freely around the Reference to the capillary tip. Once Counter and Reference Electrodes are properly positioned, the Cord Grip caps should be tightened by hand. Do not use any tools to tighten the Cord Grip caps.

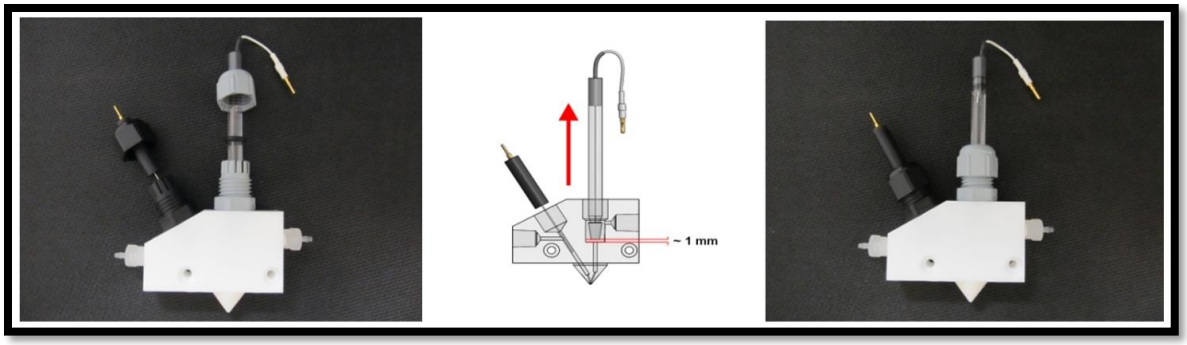


Figure 152. Positioning Electrodes in SDC Head

In the above figure (left to right), counter and reference electrodes inserted into SDC head. Positioning of Reference Electrode prior to tightening of Cord Grip cap. Cord Grip caps tightened on fully assembled SDC Head.

9.6 Pump Setup

Remove two of the cassettes from the peristaltic pump's housing. Press the release button of the cassette to be released. It should pop up and be easily removed from the pump housing. If it does not pop up from its location, lift up on the release button for the cassette. Please see photos below.

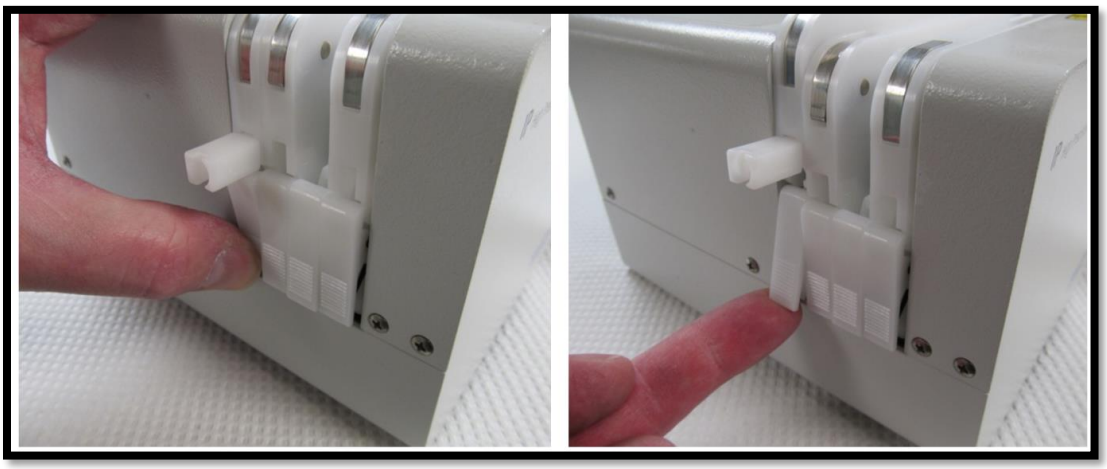


Figure 153. Steps for Releasing Cassette Button

Once the two cassettes have been removed from the pump housing, the PVC tubing sets need to be installed by stretching one PVC tubing set over each of the semi-circular cassette's end points as shown below.

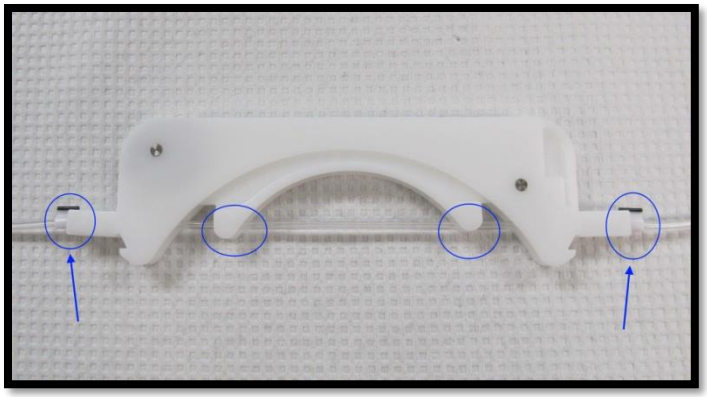


Figure 154. Peristaltic Pump Cassette with PVC Tubing Set Properly Installed

The PVC tubing set has white stops that prevent the tube from slipping once it has been secured between these end points, as indicated by the arrows. Ensure that the tabs of the white stops are aligned with the small slots in the cassette's end points. Also be certain that the PVC tubing set is aligned between the cassette's tabs in the middle of the cassette as highlighted in the circled areas. PVC tubing sets need to be installed into two cassettes, one to push liquid to the tip past the Reference Electrode and one to remove liquid from the tip and pull it past the Counter Electrode.

Once the cassettes have been prepared as above, they should be returned to the peristaltic pump housing. Insert them back into the housing one end at a time as shown in the photos below. Ensure that the bottom end of the cassette properly engages the hardware on the pump housing before pushing down the other end. Once the first end of the cassette is fully engaged in the pump housing, swing the opposite end of the cassette down towards the housing and press the cassette into the housing's hardware until it "clicks" into place.

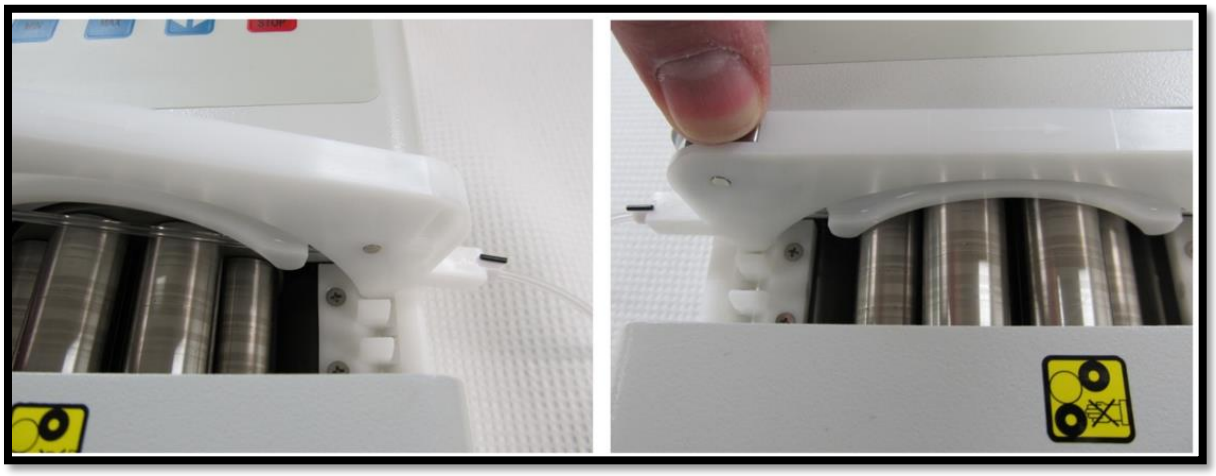


Figure 155. Steps for Reinserting Pump Cassette

NOTE The cassettes should be inserted into the pump such that the metal clips on them are all on the same end. The arrows on the caseates which indicate the direction of the solution flow should all be facing the same direction.

It is important to locate the peristaltic pump close to the scanning head and route the input and output PVC tubing from the peristaltic pump to and from the PTFE SDC Head such that the tubing will not become entangled while the SDC Head is in motion. Ensure which tube will be feeding liquid to the SDC Head and which is to be pulling liquid away from the tip. Once the tubes have been identified, connect the input and output tubes to the appropriate Bayonet connectors on the SDC Head. It will be helpful to reference the SDC Principle of Operation section of the manual for further details on the flow schematics to ensure the tubing is routed properly.



Figure 156. Tubing Connected to SDC Head

In the image above, the connection on the left side is the outlet that drains to waste. The connection on the right side is the inlet from the solution reservoir.

> **NOTE** It is often easier, especially with new tubing, to attach the tubing to the Inlet and Outlet Bayonet Hose connectors when the SDC Head is dismounted from the Stage. Ensure that the end of the tube is pushed as fully onto the Bayonet Hose connector as possible. A small piece of fine grit sandpaper is very helpful to provide additional “grip” on the tubing to assist in pushing it over the Bayonet connector. Take care to not kink or otherwise damage the Bayonet connector or the tubing when inserting it onto the connector. Damage to either the connector or the tubing may result in leakage of the liquid from the tubing or drawing air into the tubing. Either of these issues will make maintaining a consistent drop at the tip VERY difficult.

If the SDC Head was dismounted from the Stage to attach the tubing to the Inlet and Outlet connections, remount it to the Stage now.

Once the above steps are completed, connect the Potentiostat’s Cell Cable to the SDC head and the Standard Sample. Connect the White Reference lead to the Reference Electrode (RE) on the right side of the SDC Head and the Red Counter Electrode lead to the Counter Electrode (CE) on the left side of the SDC Head. Ensure that the Green Working lead is plugged into the Grey Sense lead. These combined leads form the Working Electrode (WE) lead which should be connected to the Sample. Connection to the Sample is made via the wire that is hanging out of the bottom of the L-Cell’s Cord Grip under the L-Cell’s Base.

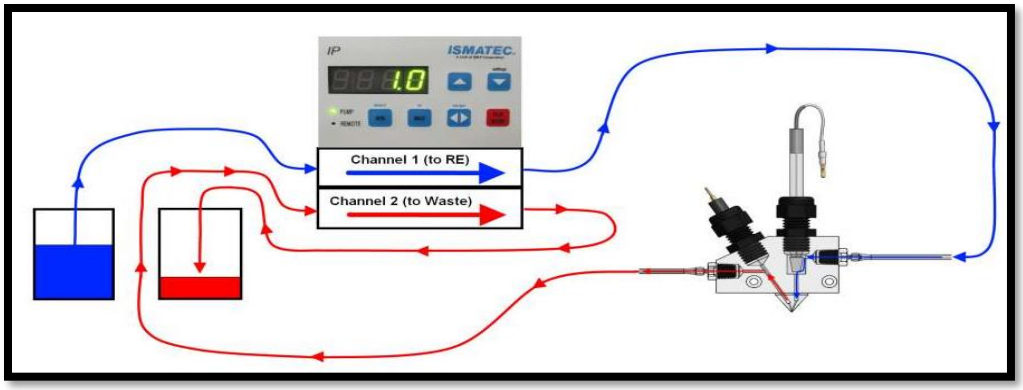


Figure 157. General Schematic of Liquid Flow Through the SDC System

In the image above, Channel 1 and the blue lines represent the "fresh" solution being carried to the SDC Head flowing into the side containing the RE. Channel 2 and the red lines represent the solution being pulled to the waste.

The image below illustrates the PTFE SDC Head and its internal channels in a semi-transparent format. The electrodes are also shown to illustrate the mechanism of the solution flow via the Head's channels past the electrodes. The solution is input through the bayonet connector on the right-hand side of the picture, passing by the Reference Electrode's frit before descending to the tip via a capillary (Flow path illustrated by blue arrows). The return path from the tip is via the left-hand capillary past the Platinum wire Counter Electrode (CE) and out through the left-hand side bayonet connector (Flow path illustrated by red arrows). If all fittings were properly sealed and installed and all seals remain airtight, the solution's path should be uninterrupted by air bubbles.

IMPORTANT Air entering the SDC Head at any of the various sealing points can make Flow Balancing and maintaining a consistent drop at the tip very difficult.

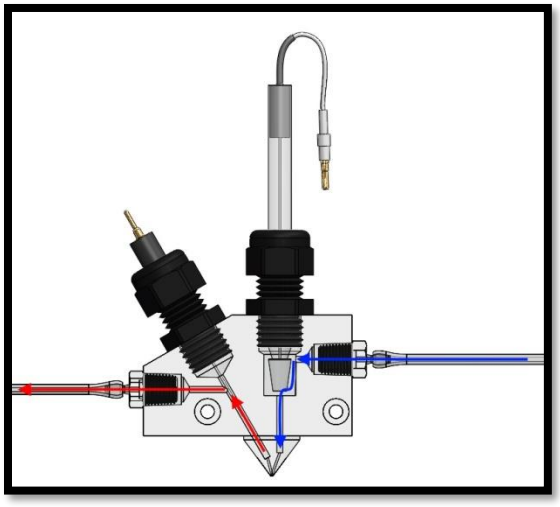


Figure 158. Semi-Transparent View of SDC Head and Solution Flow Path

A closer examination of the SDC Head's tip in the image below illustrates how the continuous flow of solution refreshes the micro-cell of fluid within the drop at the tip as 'fresh' solution (blue) enters the micro-cell and 'reacted' solution (red) is removed from the surface of the sample. This is possible due to a balance flow of solution being "pushed" in towards the SDC Head at the same rate at which solution is being "pulled" away from the SDC Head by the peristaltic pump.

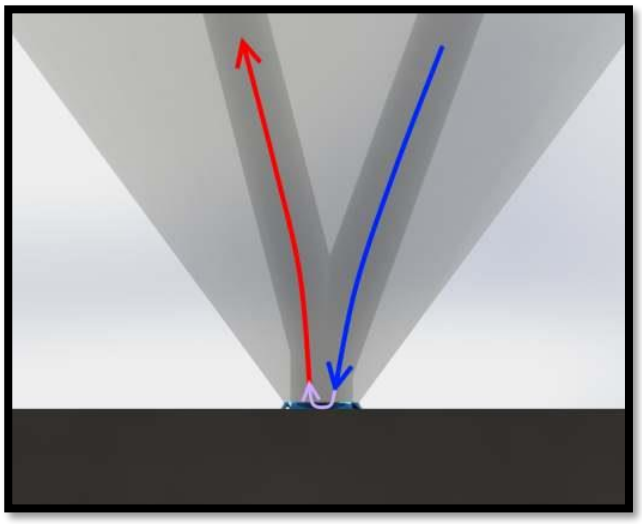


Figure 159. Closeup of SDC Head's Tip

The image above shows details of SDC Head, and the "micro cell" formed between the tip and the sample surface in a continuously refreshed droplet of solution.

A typical SDC experiment scans the micro-fluidic cell (droplet) across the sample's surface allowing one to create a map of the distribution of Current or Potential on that sample. The scan is usually performed via a raster in the X or Y lines or the X&Y plane. The magnitude of the measured probe Current or Potential is synchronized with the specific X-Y probe position. From this, the system builds a quantifiable map of the Current or Potential distribution across the surface of the sample. The SDC technique uses a Potentiostat which provides the ability to both measure and control the conditions as defined by the user. The signals generated by the experiment are acquired by the PC for analysis and storage.

The SDC Standard Sample Test procedure measures the current flow for a constant -500 mV potential versus Ag/AgCl in a 0.1 M KCl solution, highly conductive at 13.5 mS/cm. When the SDC tip is over the epoxy area of the Sample, the resin acts as a high-quality insulator thereby preventing any charge-transfer through this material to the Working Electrode. As a result, the current measured is relatively small. When the tip moves over an Au area, the charge-transfer occurs at a much higher rate resulting in a measurable flow of current.

9.7 SDC Flow Balancing

NOTE Flow Balancing must be adjusted for each new sample being tested or any time the SDC Head has been moved away from the sample in the Z axis.

While SDC can be performed without solution flow, the SDC technique usually relies on balancing flows of solution to and from the SDC Head during an experiment. Depending on the sample and/or specific setup details, this can appear to be difficult to achieve. The following is intended as a general guideline covering the most common areas a user should investigate to balance the flow and maximize results and success of the overall experiment. The topics discussed are based upon experience with the SDC technique and should aid in common flow balancing problems.

The following topics are targeted towards reduction of out-welling of solution from the tip – this is evident when more solution is flowing to the SDC Head than from it. If the case is the opposite to this scenario, i.e. no solution appears to meet the sample as all solution is immediately drawn up the return capillary, check that there are no blockages in the system, ensure that there are no air leaks (by re-doing the PTFE-taped joints) and finally, temporarily squeeze the return tubing with finger/thumb long enough until some solution is forced onto the sample. Often, once the solution meets the sample's surface it will remain in contact.

9.7.1 The Connections

It is extremely important to make sure there are no air leaks in the system as air bubbles can make it very difficult (if not impossible) to maintain an adequate contact of solution to the sample and electrodes. The best way to avoid such air leaks is to properly seal each of the threaded joints connecting to the SDC Head with PTFE tape as shown in the "Using the VersaSCAN in SDC Mode" section of the manual. This should always be the first step in setting up the SDC head. All old PTFE tape should be removed any time a threaded component has been extracted from the assembly. If any air leaks are suspected, retape all joints.

9.7.2 The Sample

While many kinds of samples can be analyzed with SDC, not all sample types are suitable for use with the SDC technique. Specifically, it is recommended that the sample be hydrophobic to some extent. If the liquid is absorbed/drawn up by the sample, scanning a droplet over the sample will leave trails of solution behind and possibly obscure the results. However, it may still be possible to perform point-wise measurements on such hydrophilic samples.

One obvious change to most sample surfaces that will deteriorate the SDC Head performance (in terms of its ability to properly confine solution in a droplet) is wetting the sample's surface. This can especially occur during the set-up process when solution wells out from the tip leaving the sample surface wet in the area adjacent to the tip. If most of the welled-out solution is removed but the surface remains wet, it is very likely that the out welling will recur immediately, whether or not the flows are properly balanced.

9.7.3 The Pump

While the peristaltic pump should, in principle, flow the exact volume of solution from all channels simultaneously, wear and/or manufacturing tolerances in the pump rotors, individual cassettes, and/or tubing sets may allow for slight differences in either the flow rate and/or solution pressure within the system. Any subtle differences in any of these components can cause out welling of the solution at the tip on the sample's surface.

A common cause of flow balancing issues is the use of old PVC tubing that has been left installed in the peristaltic pump for an extended period of time. This causes the tubing to become deformed at the point where the pump rotor has remained in contact with the tubing. In such cases, the pump will often provide an audible “warning” that there is a problem: a periodic “thumping” sound may be heard as the rotor moves across the tubing’s deformed point(s). If the peristaltic pump is not quiet, or has a regular beating rhythm, it is very likely necessary to replace the PVC tubing set(s) in the cassettes.

Further remedial action could utilize any one of the following or a combination:

- Swap the input PVC tubing with the output PVC tubing – specifically, the PVC tubing that has the white stops to secure it within the peristaltic pump cassette. See the “Using the VersaSCAN in SDC Mode” section of the manual for guidance on how to remove and reinstall the pump cassettes. Swap the PVC tubing set from one cassette with the PVC tubing set held in the other cassette, keeping the cassettes themselves in the same location in the pump housing.

- Swap the two peristaltic pump cassette positions providing input and output flow, this time keeping the PVC tubing with their respective cassettes. If this still does not rectify the issue, try swapping the tubing again as explained above.

9.7.4 The SDC Reference Electrode

The distance between the Reference Electrode (RE) and its seat can be a defining factor for the flow of the solution through the SDC Head. It is quite possible to block the flow by inserting the RE into a position that blocks the seat. Such blockage is usually evident when running the pump as the flow of any small bubbles from the peristaltic pump to the SDC Head becomes cyclic rather than in the direction of (towards) the SDC Head.

However, if the gap between the RE and its seat is too large, a small well or volume of solution can form in this area, which can make balancing the flow from the pump difficult to manage.

The RE should be inserted as fully as possible without blocking the solution path. If other methods have failed in balancing the flow, try readjusting the position of the RE, ensuring that the RE is not pressed against the seat and that a gap of ~ 1 mm is in place between the bottom of the RE and the seat. Instructions on positioning the RE can be found in the “Using the VersaSCAN in SDC Mode” section of the manual.

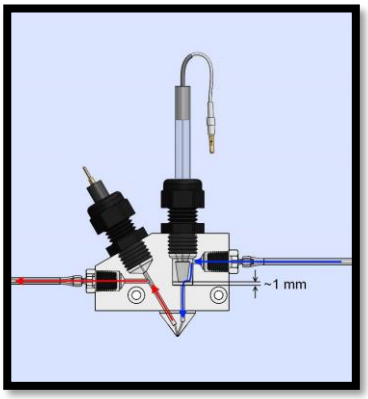


Figure 160. Proper Positioning of Reference Electrode in SDC Head

9.7.5 SDC Head Positioning

The proximity of the SDC Head to the sample is also a key to achieving a reliable solution volume at the tip. The further the SDC tip is from the sample, the less of an effect surface tension will have on constraining the solution to the tip locality. If flow appears to be approximately balanced to the tip, yet difficulties remain in keeping the flow balanced, try bringing the tip steadily closer to the sample in 20-micron increments. At each increment, dry the sample surface due to any prior out welling (using tissue paper) and wait a brief period of time to see if the issue is resolved. Remember that once the sample is wet, it is much easier for out welling to recur. Depending on the solution and sample properties, running the SDC Head in contact with the sample may be required.

9.7.6 Tube Clamps

Partially clamping the PVC tubes to and from the peristaltic pump is an option that offers a further degree of control for balancing, although it should not be used as a cure-all. If reasonable attempts are made to balance the flow via the other previously mentioned approaches, it is often not necessary to use the tube clamps in many cases while they will only provide a minimal influence in others if used as a last means of balancing the flow. Properly locating the clamps is important. **Similarly, placing the clamps improperly can lead to MORE problems including air bubbles and leaks in the system.**

The following advice is offered:

- Referring to the image below, the best location for the tube clamp is between the "fresh" solution reservoir and pump "Channel 1 (to RE)". If necessary, an additional clamp (not shown) can be placed between "Channel 1 (to RE)" and the SDC Head. Keep in mind that it is easier to prevent the SDC peristaltic pump from pulling solution from the source than it is to prevent it from pushing solution to the head. It will take some practice and experimenting to find the best solution for the specific situation.

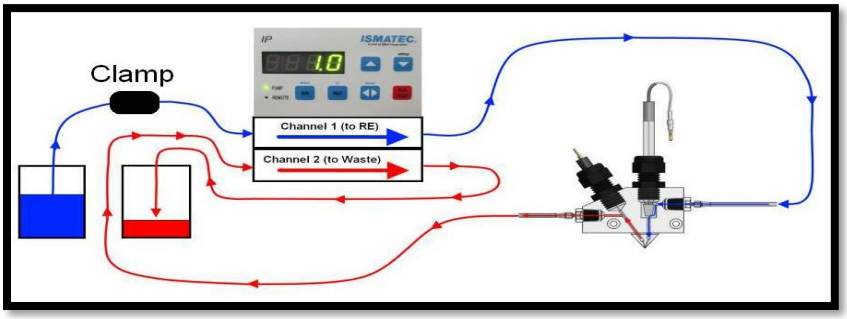


Figure 161. Proper Clamp Location

- When attempting to balance the solution flow by using tube clamps, a useful method is to move the SDC Head completely away from the sample (prior to doing so, note its approximate X/Y/Z locations to make its later return to the sample easier) so that the SDC Head is in free air. Place some paper towels or tissue wipes under the tip to catch any drops that may fall. Running the pump first with the tube clamp(s) fully unclamped will likely produce drops of solution at the SDC Head's tip, which will then grow to the point that their size will cause them to fall.

Once drops are falling from the tip, adjust the tube clamp(s) slowly and carefully until the solution drop at the tip remains the same size, neither expanding nor contracting. Once this steady state is achieved, the flows are balanced and the SDC Head can be returned to the sample. This technique can be a useful way of avoiding unnecessary out welling of the solution at the tip while adjusting the flows. Remember that out welling leads to unwanted wetting of the nearby sample surface which will make droplet confinement difficult.

9.8 SDC Pump Calibration

> **NOTE** Pump Calibration can be repeated as necessary/desired to ensure proper flow delivery during the experiment. One reason for the Pump Calibration process is to ascertain if the PVC Tubing needs to be replaced. The tubing does require periodic replacement dependent upon amount of usage and how it's maintained to ensure optimal performance.

- **Periodically check the ends of the PVC tubing for signs of hardening, cracking, splitting, or other damage and ensure that the PVC tubing ends are seated fully and properly onto their Bayonet fittings.**
- **Periodically check the PVC tubing in the cassettes where contact is made with the rollers for signs of stretching/wear over time. It will be necessary to first remove the cassettes from the peristaltic pump housing to accomplish this.**

Arrange the pump and the SDC fluidics system as described in the "Using the VersaSCAN in SDC Mode" section of the manual and approach the sample surface as described in "Running the SDC Test Sample" section.

Fill a beaker with a reasonable amount of deionized water, sufficient to run several pump calibration experiments, and insert the PVC tube that will draw solution from this reservoir. Use a graduated cylinder with fine graduations and place the output PVC tube into it. The scheme should be arranged similar to the image below:

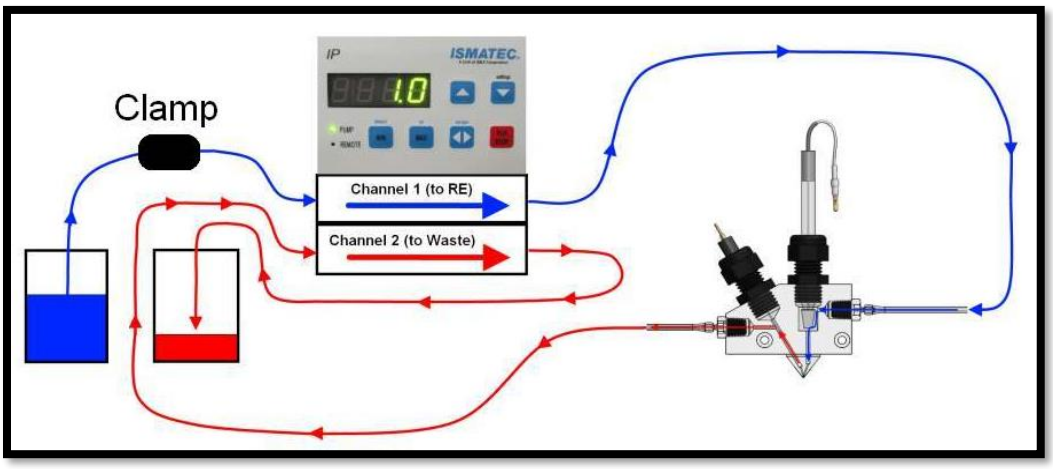


Figure 162. General Flow Schematic for SDC System

For Pump Calibration, the Graduated Cylinder should be used in place of the red "Waste" vessel to receive the output from "Channel 2".

After everything is set up as described above, run the SDC system for several minutes to ensure that liquid does not pool at the SDC tip. If necessary, utilize the techniques described in the "Flow Balancing" portion of the manual to balance the flows. Ensure that there are no persistent leaks in the system.
Once the system appears to be operating correctly, stop the peristaltic pump and completely empty the graduated cylinder of its contents.

Select a number of flow rates that will help calibrate the pump across the interest range.

Set the flow rate with the peristaltic pump's interface (see image below) and time the interval in which it takes to flow a set volume, or measure the volume flowed in a set time, as shown below. Note this and repeat for all the other selected flow rates.



Figure 163. Peristaltic Pump Interface

The Flow Rate is increased or decreased by pressing "UP" or "DOWN" arrows as desired. Arrows are highlighted in a red circle in the image above.

Create a plot of these results to generate an approximation of the pump flow calibration via a straight-line fit.

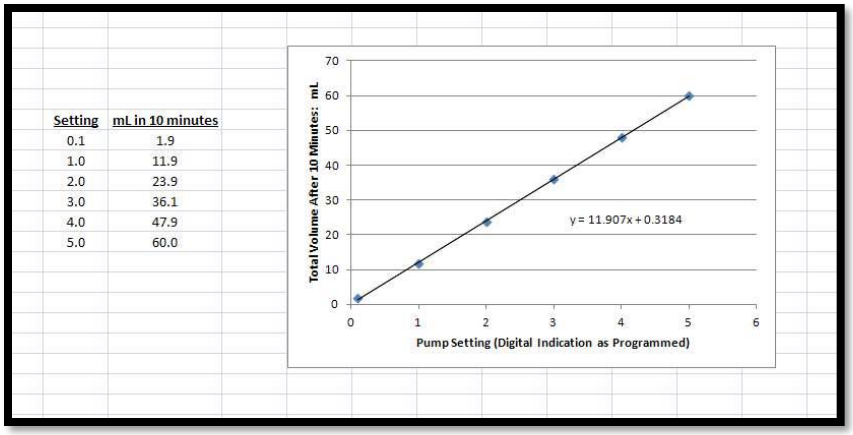


Figure 164. Flow Calibration Example

In the image above, note that the user's flow conditions may be different. This is only an example.

Use of this method prior to the experiments will ensure an exact volume of solution is flowing.

9.9 Reference Electrode

When a new Reference Electrode (RE) is first received, it arrives with a protective sheath on it to seal the frit/junction preventing internal filling solution from draining and the frit/junction from drying out while the electrode is being shipped or stored.

This sheath must be removed prior to the RE being used, otherwise it will not function. It is equally important that the sheath is properly removed to not damage the frit/junction on the RE which would also cause the RE to not function properly. No tools should be used to remove or cut the sheath from the RE.

Please see the photos below for proper sheath removal from the RE.

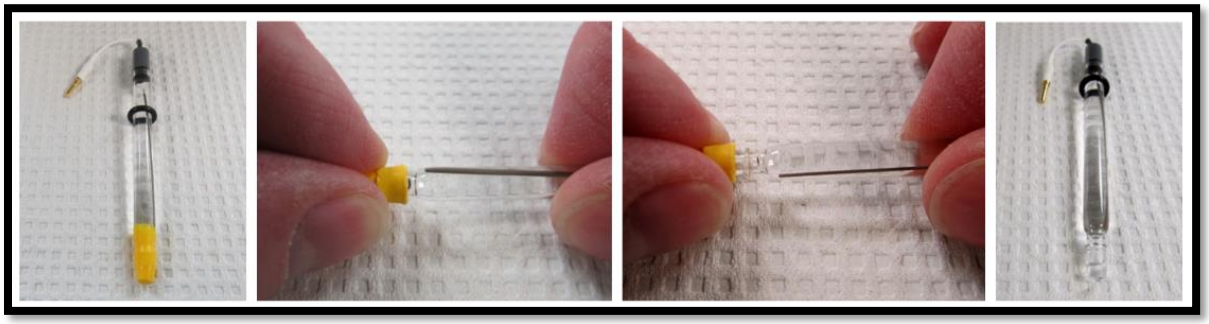


Figure 165. Removing the Reference Electrode Sheath

CAUTION: The Vycor frit/junction is attached to the end of the RE with Teflon heat shrink tubing. If too much force is used to remove the sheath, the Vycor frit can be detached. The RE will NOT function properly if this occurs. Use care while removing the sheath.

Once the sheath has been removed, the RE should be inspected to ensure that the frit does not appear to be damaged. Further, the RE should be inspected for bubbles lodged in or near the tip.

CAUTION: Use of a Reference Electrode with bubbles lodged in the tip will prevent proper electrical contact with the sample solution. This disruption in the electrical circuit can lead to damage to the Working Electrode along with Overloads in the Potentiostat.

Please see the photos below illustrating the inspection of the RE following removal of the sheath.

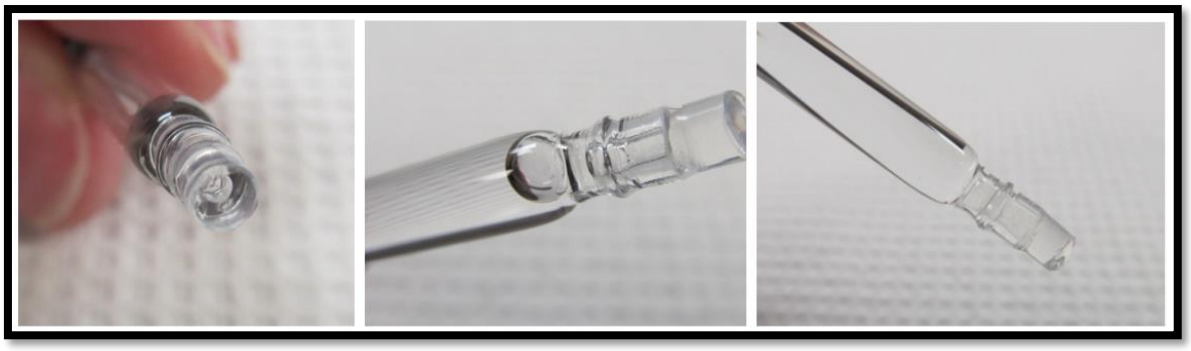


Figure 166. Inspection of Frit

In the image above from left to right: Inspection of frit to ensure no large cracks / chips. Checking for bubbles at or near RE's tip – this example has a large bubble near the tip AND a large bubble along the length of the tip. Appearance of the same RE after carefully dislodging any bubbles.

The RE's frit should have no large defects noticeable in it. Apart from this, it is very important to check the tip of the RE for bubbles. If bubbles are found within the tip of the electrode, hold the electrode with the tip facing down and carefully tap the bottom portion of the electrode body being careful not to touch the frit. Repeat tapping until no bubbles can be seen at the tip of the electrode. Any bubbles that are dislodged will float to the top of the RE and will not pose any problem in that location.

It is important to properly store the RE when not in use and to not allow the RE's frit to ever dry out. The RE used with the VersaSCAN should be stored in a vessel containing 3M NaCl once its sheath has been removed. Do NOT store the RE in water only.

Proper maintenance and storage of the RE are critical for proper operation of the various VersaSCAN options that require usage of an RE. A poorly maintained, damaged, or RE otherwise requiring replacement will lead to noisy data, oscillations, overloads, and/or damage to the Working Electrode.

9.10 VSC-SDC System Test Procedure for Gold Disk Test Sample

Prior to running this procedure, the VersaSCAN must be configured for the SDC System as described in the "Using the VersaSCAN in SDC Mode" section of the manual. It will also be very useful to review the section entitled "SDC Principle of Operation" prior to running this test.

The SDC Standard Test Sample consists of a 5mm Au disk mounted and set in an epoxy mold. The purpose of this test sample is to allow the user a way to verify that all of the various system components are functioning properly by performing a simple electrochemical measurement under known conditions. This same test sample is used to demonstrate the SECM technique.

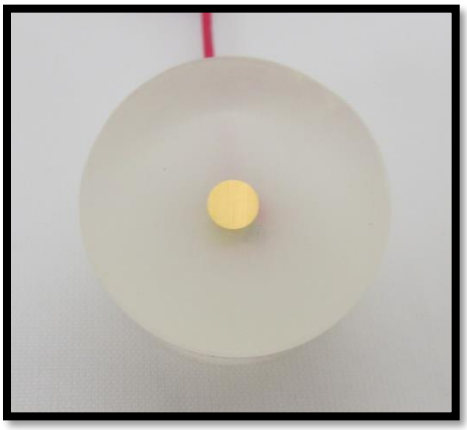


Figure 167. SDC (and SECM) Standard Test Sample

Once the VersaSCAN System is fully configured and ready to run in SDC Mode, use the manual stage controls 

to maneuver the SDC Head's tip to a close proximity to the surface. The SDC Standard Test Sample must be polished prior to testing. When properly polished, the test sample will appear somewhat shiny and will give a slight reflection of the SDC Head's tip as it approaches the sample. This can be useful as an aid to get the tip close to the surface in conjunction with the image on the VersaCAM's LCD Monitor. The SDC Head should be positioned such that the tip is in the middle and at the left of the sample, which is the position required to be ready to perform an SDC area scan.

If the VersaCAM option was purchased with the instrument, focus the video camera such that the view is just of both the tip of the SDC Head and also the sample surface. Providing additional lighting may be of help when setting up the SDC equipment, especially if the environment is poorly illuminated.

NOTE Some light sources can cause excessive noise within the measurements, especially arc-lamps, fluorescent bulbs. Do not use these during data acquisition.



Figure 168. VersaCAM Camera Showing the Head Being Brought Towards the Sample

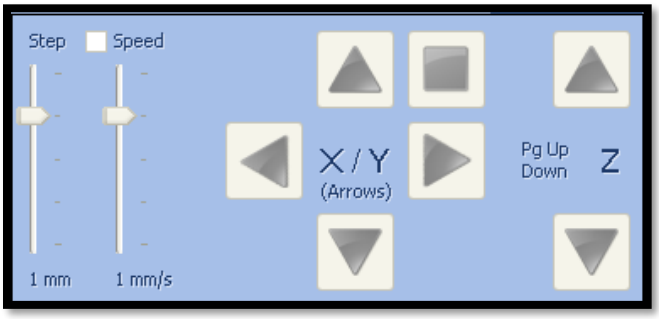


Figure 169. VersaSCAN's Software Manual Control for Stage Movement

When the SDC Head is located too far from the sample surface, the liquid being pumped to the tip will likely well out from the tip covering more surface area than it would if the tip were ideally located very close to the surface. Further, when the SDC Head is too far away from the sample surface, the feed solution from the peristaltic pump input may not refresh the pooled liquid at the tip as efficiently versus if it were properly located. The degree of out welling of liquid around the tip will also be affected by the solution's viscosity and the surface's degree of hydrophobicity. Experimentation with the sample, the solution and the tip-to-surface distance will help users understand the tip-surface requirements for an SDC experiment. Several helpful hints on balancing the flow can be found in the "Flow Balancing" section of the manual.

For the SDC test sample, the solution to be used is 100mM KCl^{-} solution. This gives a conductivity reading of ~ 13.5mS/cm. This is simply achieved by mixing 7.45g of potassium chloride (KCl^{-}) into 1 Liter of deionized water, although in practice, much smaller volumes are required.

Place the input and output pipes of the dual channel peristaltic pump into a beaker containing this solution and turn on the pump at approximately 1mL/minute pump rate. (See SDC Pump Calibration section for pump calibration information.) Users should immediately see the solution being pulled into the silicone tube on one side and drops emerging from the other tube.

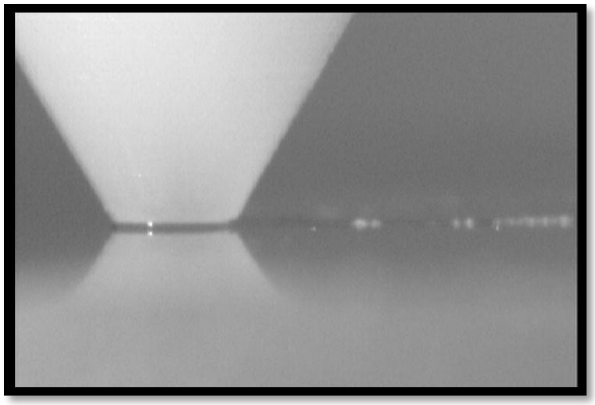


Figure 170. SDC Head in Close Proximity to the Sample Forming a Liquid "Microcell"

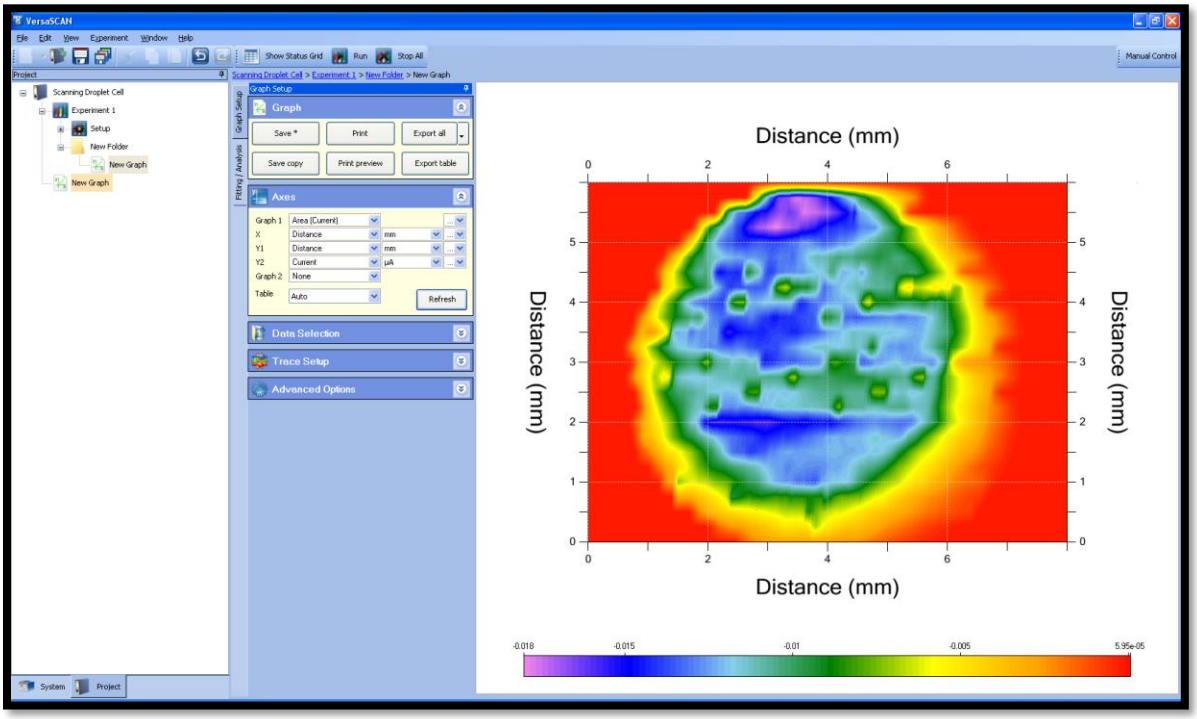


Figure 171. SDC Test Showing SDC Results Over the Whole 5mm Au SDC Test Sample

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10. VERSASCAN OPTICAL SURFACE PROFILING (VSC-OSP)

10.1 OSP Technique Overview and Introduction

The goal of the Optical Surfacing Profiling measurement is to measure the topography (height differences in Z) of a sample. This is a laser-based measurement which is generally made in air, but under the correct conditions could be made through liquid electrolyte.

The OSP laser head has an LED on it that serves as a color-based range detector.

The user should be able to independently set the Scan Distance and Point Density (size of pixel) in both X and Y for an Area Map. The user should be able to set Scan Speed in a SWEEP mode. The user should be able to set Delay, Samples, and Acq Freq for STEP mode.

OSP experiments are typically high data density and faster scan speeds. (There is no electrolyte to stir or logic loops to confuse.)

Data should have X coordinate as Sensor position, Y coordinate as Sensor position.

The Topographic Output from the Sensor should be recorded and displayed in the Data Map.

The measurement range of the OSP Sensor is 10-mm. The laser is estimated to give a topographic resolution of 1-2 microns.

10.2 Applications

Data generated from these experiments are often used for these applications –

1. A method to quantify topographic changes and correlate those changes to electrochemical data acquired by another method. Specific example is to measure the geographic dimensions of a “pit” local corrosion site and use SVP to measure the electrochemical intensity of that active corrosion event.

2. Use the acquired topographic data as a background file from which the probe of an electrochemical technique is incremented in Z to maintain a Constant Probe-to-Sample Distance during an Area Scan data map. “Constant Distance” experiment removes convolution from topographic changes to electrochemical data. This only ensures a Constant Distance and is not a mechanism for setting probe-to-sample distance. These experiments require much effort and are reserved for truly complex topographies (beyond tilt or surface roughness, but actual curvatures).

3. Use as a high degree level to manually adjust the tilt of the sample prior to an electrochemical experiment.

10.3 VSC-OSP Packing List

Table 18. VSC-OSP Packing List

Description	Ametek PN	Quantity (Each)
Potentiostats		
VSC-OSP Laser Head	233734	1
VSC-OSP Laser Controller	233735	1
Cable, 2M, VSC-OSP to VersaSCAN System Box	233736	1
System Control Box and Internal Assemblies		
VersaSCAN System Control Assy	224118-PT	1
VersaSCAN Sys Box Cable Assy, Laser Controller	224151	1
VersaSCAN Laser CNTRL Bracket	224132	1
VersaSCAN CBL Assy, Laser Contr INTFC	224141	1
Probe Mount Hardware		
VersaSCAN OSP Probe Mount	224058	1
VersaSCAN OSP Laser Mount	224059	1
VersaSCAN Probe Holder, 4mm	224062	1
Bracket Mounting Hardware		
End Clamp, Post, M6	233739	2
Optical Post 100mm	233740	2
Optical Post 150mm	233741	2
Clamp, 90 deg	233742	2
Test Samples		
VersaSCAN Slip Gauge Test Sample, 10mm	233732	1
VersaSCAN Slip Gauge Test Sample, 5mm	233833	1
VersaSCAN Slip Gauge Test Sample, 1mm	233834	1
Connectivity and Power		
Extension Cord	803937	1
Cable, Trigger, SMA-BNC, 1m	1116486	1

10.4 Cable Connections for VSC-OSP

> **NOTE** If the system has TWO motion controller boxes, please refer to Appendix 1 for set-up diagrams.

The diagrams are additionally available as part of the "Setup" of each experiment.



Figure 172. OSP Setup Diagram

The external cable connections for the VSC-OSP are straight-forward.

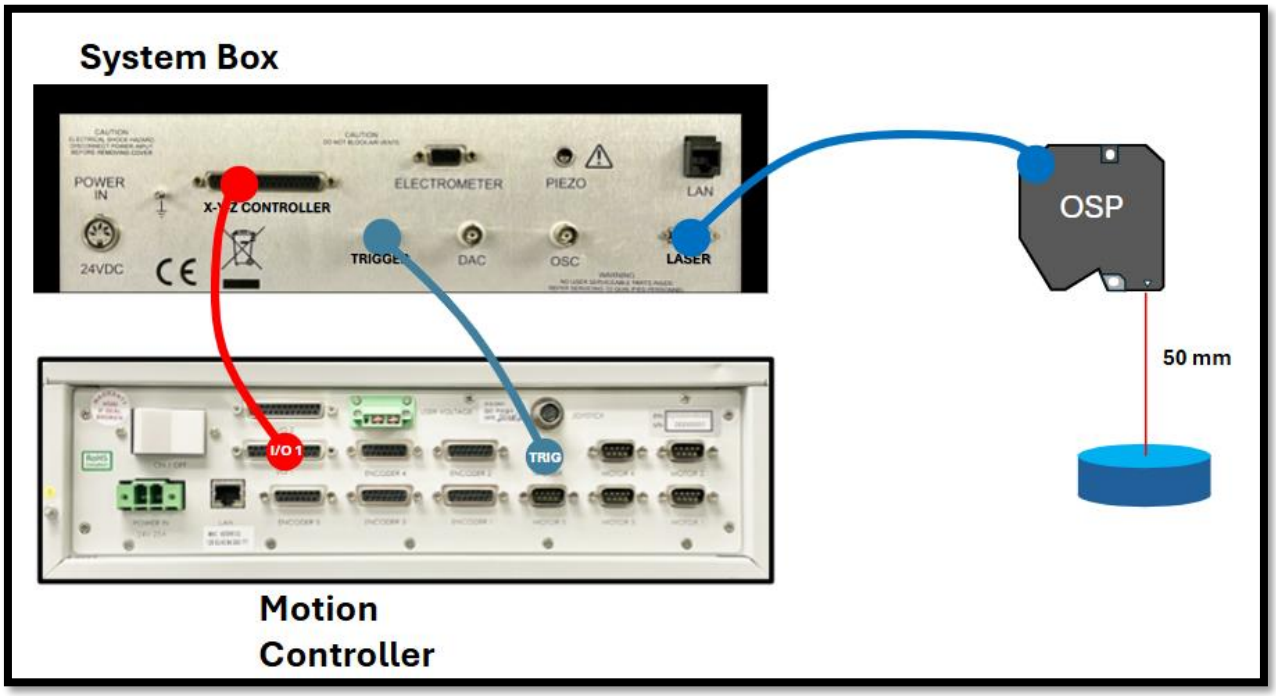


Figure 173. OSP Cable Connections

There is a single interface cable that connects the VersaSCAN System Control Box (P/N 224118-PT) to VSC-OSP laser head (P/N 233734).

Additionally, there is a standard Ethernet cable connected from “LAN” port on the VersaSCAN System Control Box to the Ethernet Hub of the VersaSCAN system.

10.5 Software Control for VSC-OSP

10.5.1 Comments

Any comments that need to be stored with the data file can be entered into this field.

Please note that all the Scan and Measurement parameters from the experiments are already stored in each data file, so those are not necessary to be entered here.

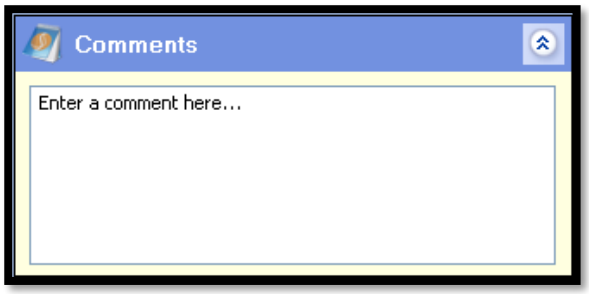


Figure 174. Comment Field

10.5.2 Conditioning

The conditioning tab allows the user to set the time for the system to be delayed before any measurement in the Step is started. Note this programmed delay occurs once before the experiment starts. The Measurement and Delay window allows other specific delays between each line and between each point to be programmed. The units for the description of time are also selectable.



Figure 175. Conditioning Tab

10.5.3 Scan Setup

Scan Setup is a generic tab that has a familiar look and feel in all the techniques.

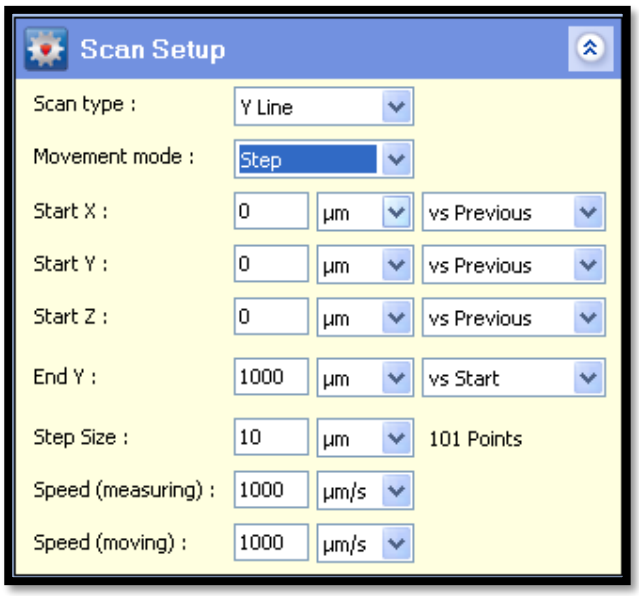


Figure 176. Scan Setup

10.5.3.1 Scan Type

The "Scan type" allows the user to define if the experiment is going to be executed in a single line axis or in an area as a series of line experiments. "X Line" would be a single line of data in X, while maintaining a constant Y and Z position. "Y-Line" scans in Y as "Z Line" scans in Z.

"XY Area" will map an Area in the XY plane. This is accomplished by a series of X scans at different Y positions. Data acquisition occurs as the probe moves from Start X to End X (e.g., for -X to +X this is left to right).

"Point" will execute the experiment without moving the probe.

10.5.3.2 Measurement Mode

"STEP" will oversample and average the data. The probe moves to a given location and remains in that location for the measurement duration. Then, it moves stepwise to the new location (1 x Step Size; here 10 microns). Oversampled data collection again occurs at the new location; data is averaged and reported. This oversampling and averaging process reduces the noise in the experiment but increases the duration of the experiment.

"SWEEP" will acquire data while the probe is moving. Data is not oversampled, which decreases the overall duration of the experiment, but may affect data quality. Time Constant of the signal chain should be considered when setting the Sweep parameters, as the probe's position is changing as data is coming from the signal chain.

10.5.3.3 Start X/Y/Z

In this field, the user defines the specific position that the experiment starts.

This can be set as "vs. Previous" or "vs. Absolute".

> "vs. Previous" will allow the probe to use its current position as the origin point. In this example, 0/0/0 vs. Previous starts the experiment from the probe's current position.
>
> "vs. Absolute" will use the known extreme position in order to keep an absolute reference grid from which positions are specified. 0/0/0 would be the far left (-X) ; back (-Y) and down (-Z).

10.5.3.4 End vs. Start

In this field, the user defines the location where the experiment is terminated.

The "Start" and "End" define the distance or area over which the experiment is performed.

The dimensions of the Scan Area should be considered when Aspect Ratio of the data of the end-result.

10.5.3.5 Step Size

This field defines the data point density. A data point is acquired and recorded at every Step size. High resolution experiments would require small step size as one component.

In Area Scan, the user can define different densities in X and Y. Pixels do not have to be squares (equal X and Y) but it is recommended and set as the default.

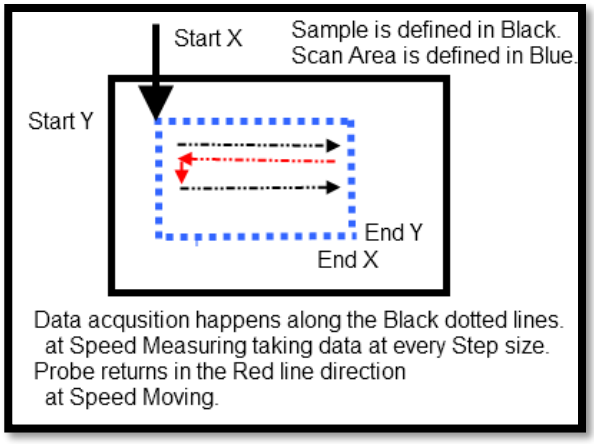


Figure 177. Area Scan

10.5.4 Measurement Mode Setup



Figure 178. Measurement and Delay

10.5.4.1 Line Delay

The Line Delay allows the user to program a set time delay between each line of data acquisition.

10.5.5 Optical Sensor Setup

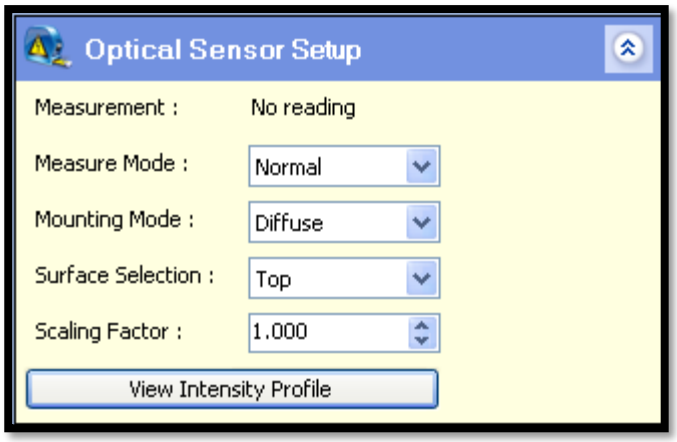


Figure 179. Optical Sensor Setup

Measurement This parameter is the measured value of the laser displacement sensor. This is the value that is recorded in the VSC-OSP experiment.

Measure Mode The VSC-OSP can be operated in Diffuse, Translucent, Transparent 1, Transparent 2, and Multi-Reflective Modes. “Normal” is the most common to measure the top surface. Other modes are for more advanced studies of multi-layer samples and environments.

Surface Selection If the more advanced Measure Modes are enabled, this parameter allows the user to set between which peaks the displacement is being measured.

Scaling Factor This parameter allows the user to adjust for any experimental or system constraints. After a standard sample, such as those supplied, is measured, adjusting this parameter allows for any corrections to the measurement value.

View Intensity Profile This displays the response from the CCD. This allows the user to correctly position the VSC-OSP head in Z to center the response in the measurement range. This provides the greatest flexibility in measuring changes in Z during the experiment. This can also graphically chart responses from complex surfaces.

10.6 VSC-OSP System Test Procedure for Slip Gauge Samples

The test samples for VSC-OSP are steel slip gauges that are machined to a specified thickness. This will test the ability of the VSC-OSP to make the measurement and ensure the measured value is correct.

1. Mount the OSP Head and connect the interface cable and Ethernet cable.
2. Power the System Control Box. Users should now see the light on the top of the OSP Head is lit indicating power.
3. In the System Tab, ensure that there is Ethernet communications with the Laser Controller.
4. With the laser head powered and an OSP Step selected in the software, users should see the red laser spot coming from the VSC-OSP Laser Head.
5. Arrange the slip-gauge test samples to measure step-height changes in the z-axis.
6. Move the VSC-OSP Laser Head in Z until the sensor on the top of the VSC-OSP Laser Head shows a Green Light. Note: The progression is Blinking Amber → Solid Amber → Green → Solid Amber → Blinking Amber.
7. Note the Measured Value in the Optical Sensor Setup.
8. Move the Head a known value in Z.
9. Use the Known Distance Movement and the changed response in measurement to determine the scaling factor and input it into the Scaling Factor parameter.
10. Users may opt to adjust the Laser Head in Z until the Measurement reads 0 microns. This is not required but will provide a nice baseline for the other values in the scan.

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11. VERSASCAN MLCELL (VSC-MLCELL)

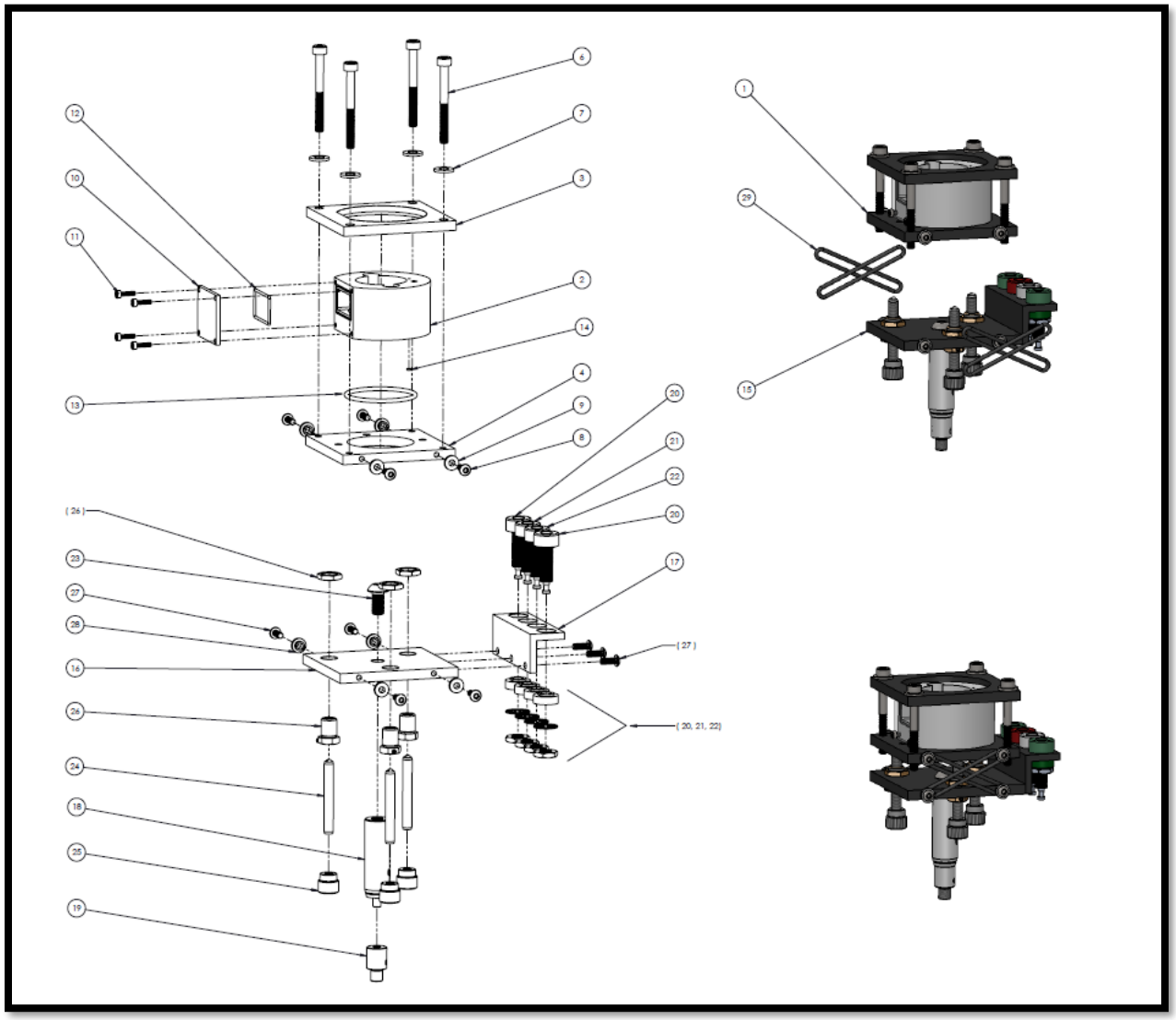


Figure 180. VSC-MLCELL Parts Diagram

Table 19. VSC-MLCELL Parts List

Item	QTY	PN	Description
1	1	224068	VSC-MLCELL Body Assembly
2	1	224040	VSC-MLCELL Reservoir
3	1	224053	VSC-MLCELL Top Plate
4	1	224054	VSC-MLCELL Bottom Plate
5	2	224055	VSC-MLCELL Sample Mount
6	4	233743	Screw M4x0.7-40
7	4	233764	Washer, Flat M4
8	4	233763	Screw M3x0.5-8mm
9	4	233762	Spacer Shoulder
10	1	224041	VSC-MLCELL Window
11	4	190182	SCREW M2x8mm
12	2	233755	O-Ring, 22mm ID, 1mm WID, Viton
13	2	233759	O-Ring, 33mm ID, 2mm WID , Buna-N
14	2	233757	O-Ring, 1/32" WID, Viton
15	1	224067	VSC-MLCELL Bracket Assembly
16	1	224056	VSC-MLCELL Stand Base
17	1	224057	VSC-MLCELL Stand Angle
18	1	233726	Post, 40mm
19	1	233725	Thread Adapter, M4 to M6
20	2	233719	Jack 4mm Banana, Green
21	1	233720	Jack 4mm Banana, Red
22	1	233721	Jack 4mm Banana, White
23	1	233779	Screw M6x1.0-12mm
24	3	233722	Screw, Precision Adjustment, 3/16-100 x 1-1/2
25	3	233724	Knob, 3/16-100
26	3	233723	Nut, Ultra-Fine Adj, 3/16-100
27	7	233763	Screw M3x-.5-8mm
28	4	233762	Space Shoulder
29	8	233754	O-Ring, 5/8" ID, 1/16" WID, Buna-N

12. VERSASCAN LCELL (VSC-LCELL)

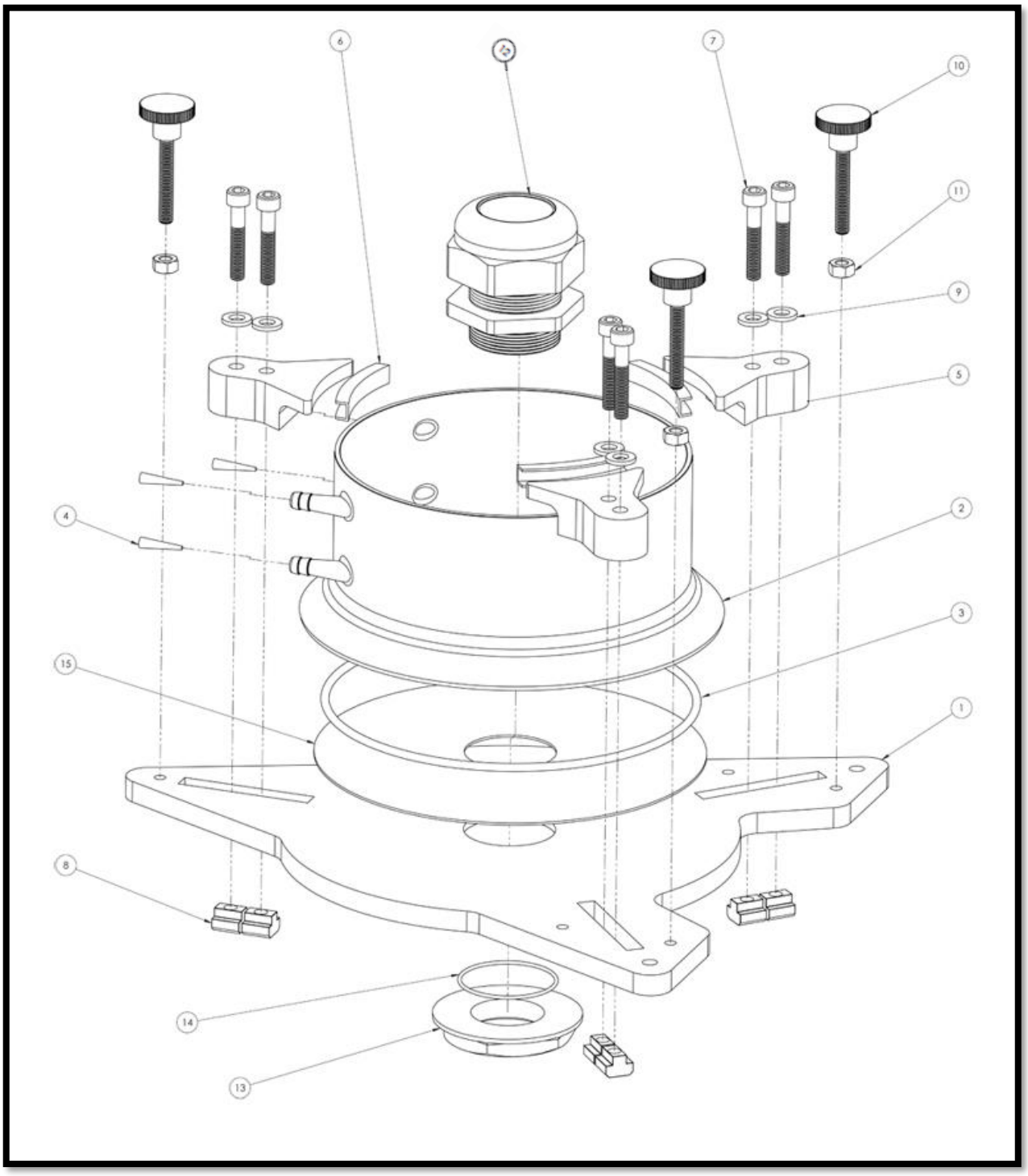


Figure 181. VSC-LCELL Parts Diagram

Table 20. VSC-LCELL Parts List

Item	QTY	PN	Description
1	1	224046	VersaSCAN Cell Base
2	1	224037	VersaSCAN Cell Tank
3	1	224047	O-Ring, 150mm Flange/-362 Viton
4	4	233717	Plug, Rubber, 1/16-3/16, ¾" LG
5	3	224047	VersaSCAN Cell Clamp
6	3	233716	Edge Trim, Polyethylene, ¼" x 9/32"
7	6	233728	Scr M6x1.0-35 SHCS 31 6SS
8	6	233714	Nut, T-Slot, M6, Nylon
9	6	233729	Washer, Flat, M6, Nylon
10	3	224730	SCR, M6x1.0 - 51 Thumb, Dog PT, 18-8SS
11	3	233731	Nut, Hex, M6, Nylon
12	1	233748	Cord Grip, M40, Standard, Nylon, Blck
13	1	233749	Nut, Lock, For M40 Cord Grip
14	1	233750	O-Ring for M40 Cord Grip, Buna-N
15	1	224052	VersaSCAN Cell Tank Washer
16	1	233835	Articulated Arm, 130mm LG, M6/M6, Blk
17	1	233836	Alligator Clip, 8-32 UNC Barrel, Steel
18	1	233837	Thread Adapter, 8-32 Ext to M6 Internal
19	1	233898	Standoff, 14" Hex, 8-32 x ¼", M/F, Nylon
20	3	233194	SCR, M6x12mm 18-8SS SHCS
21	1	224048	VersaSCAN Cell Tank Floor

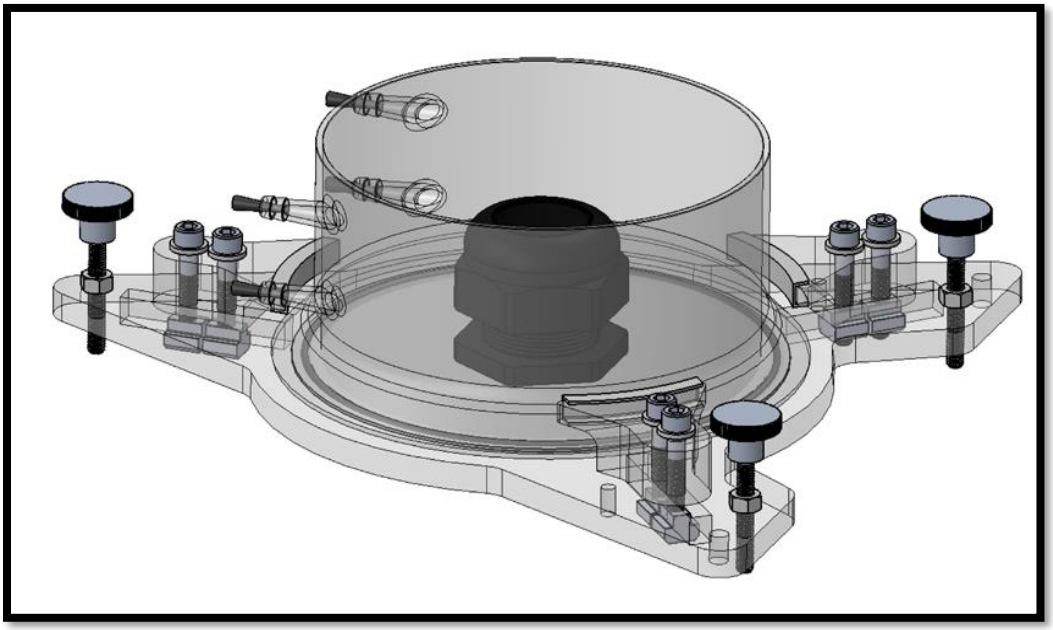


Figure 182. Complete VSC-LCELL

APPENDIX 1. SYSTEM CONNECTIONS FOR TWO STAGE MOTION CONTROLLER

The following chapter describes the system connections for two stage motion controllers. Only follow these instructions if the system has separate X/Y and Z stage motion control boxes. This applies to all units shipped BEFORE MARCH 2016 .

For reference the default IP Addresses are:

XY Controller: 192.168.10.11. Supplied with VSC-BASE.
Z Controller: 192.168.10.12. Supplied with VSC-BASE.

A.1 SECM

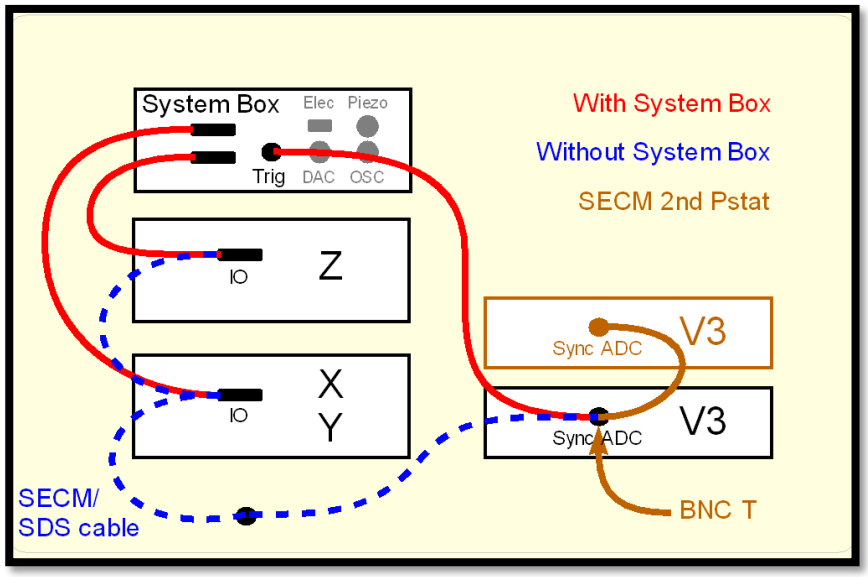


Figure 183. Connection Diagram for VSC-SECM

With System Box in Place:

Table 21. Cable Connections for VSC-SECM With System Control Box, Using Bypass Cable

OUT	IN	CABLE
Motion Controller I/O (XY)	System Box (XY)	25-Pin to 25-Pin
Motion Controller I/O (Z)	System Box (Z)	25-Pin to 25-Pin
Diff. Sync ADC (+) of V3F	T-BNC	BNC Cable
Sync ADC of V3	T-BNC	BNC Cable
T-BNC	Trig on System Box	BNC-to-BNC

Without the System Box in Place:

Table 22. Cable Connections for VSC-SECM without System Control Box

OUT	IN	CABLE
Motion Controller I/O (XY) Motion Controller I/O (Z)	T-BNC	25-Pin to 25-Pin + Pigtail BNC P/N 224145
Diff. Sync ADC (+) of V3F	T-BNC	BNC Cable
Sync ADC of V3	T-BNC	BNC Cable
T-BNC	Trig on System Box	BNC-to-BNC

A.2 LEIS

The V3F is connected to the electrochemical cell as typical.

Working (Green) + Sense (Grey) to sample
Reference (White) to the Reference electrode (Counter in a 2-electrode experiment)
Counter (Red) to the Counter electrode. Circular Pt Counter is supplied.

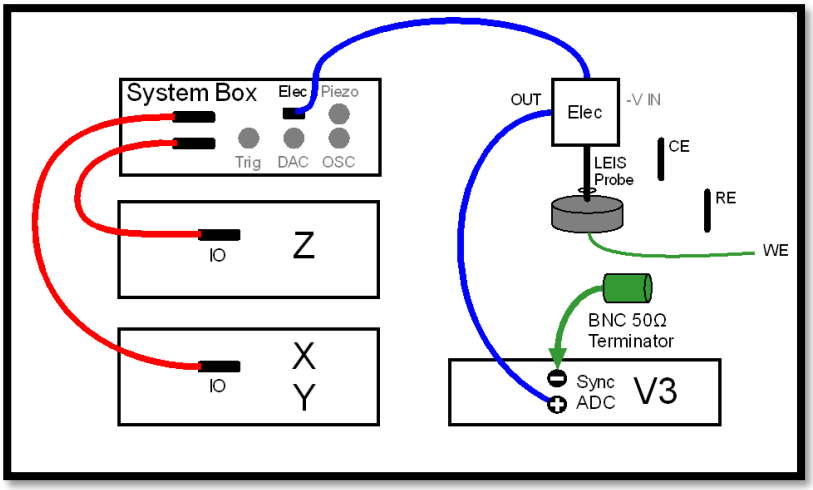


Figure 184. LEIS Cable Connections



Figure 185. V4A

A.3 SVET

Cable Connections for an Open Circuit controlled sample are below.

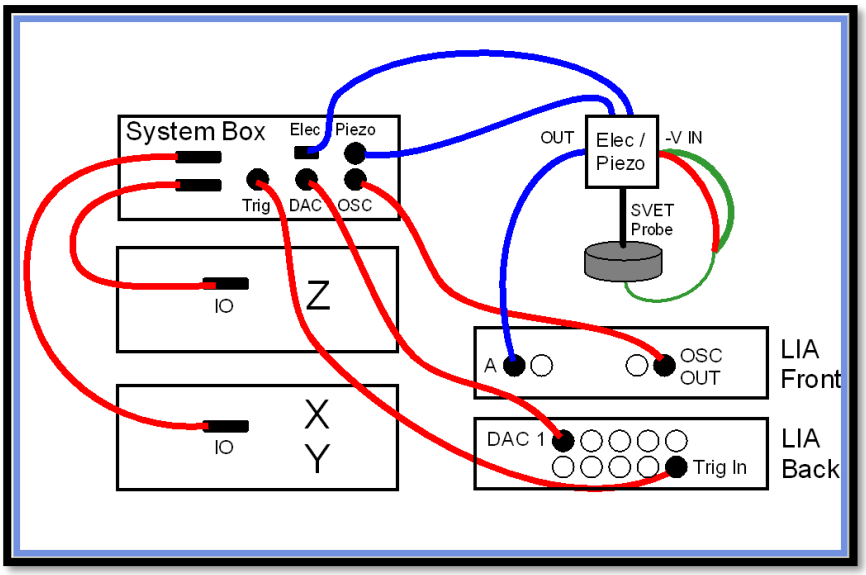


Figure 186. SVET Cable Connections for Open Circuit Controlled Sample

Cable Connections for a Galvanostatic/Potentiostatic controlled sample are below.

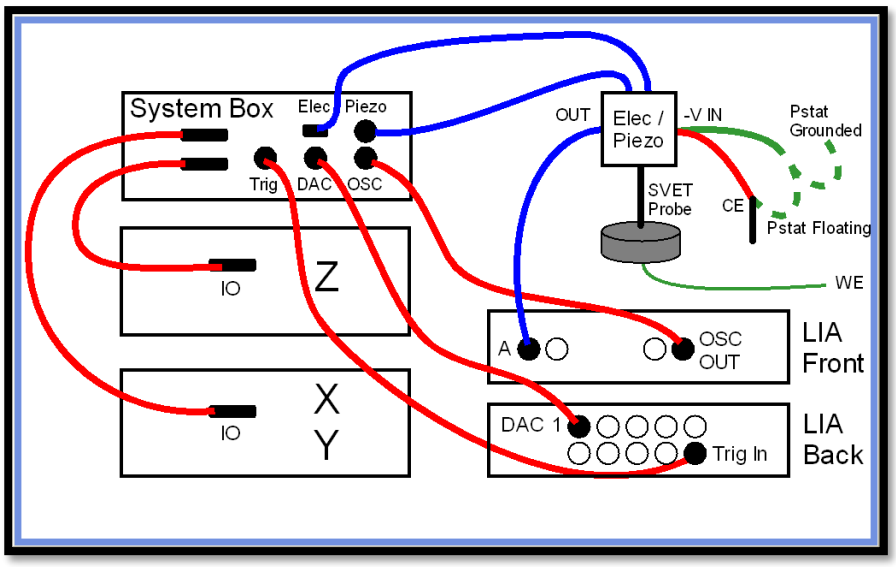


Figure 187. SVET Cable Connections for Galvanostatic/Potentiostatic Controlled Sample

A.4 SKP

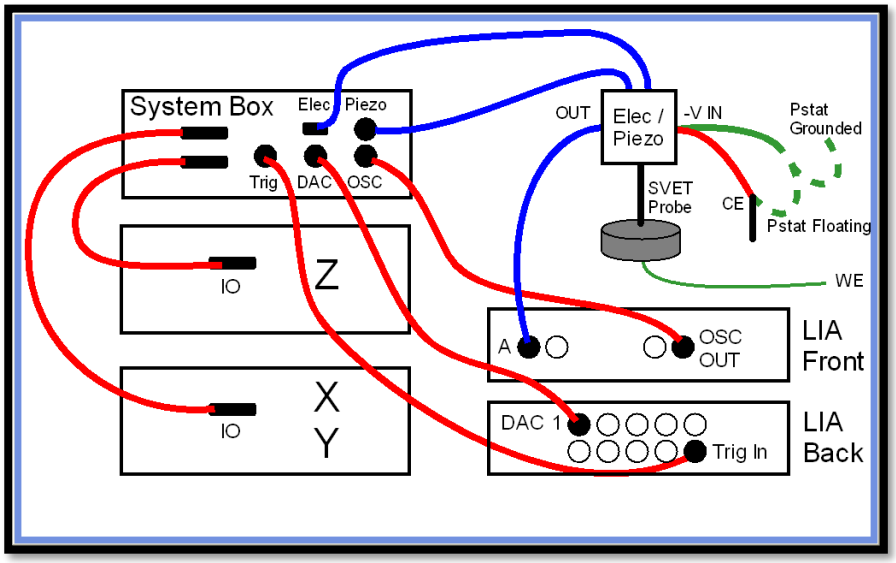


Figure 188. SKP Cable Connections

A.5 SDC

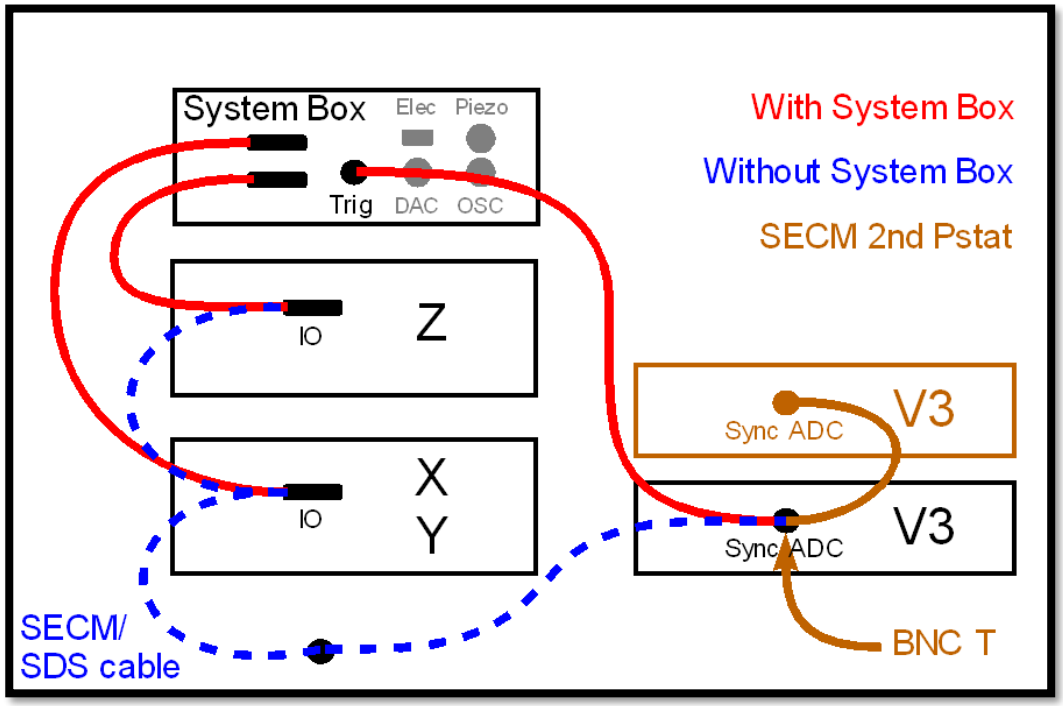


Figure 189. SDC Cable Connections

NOTES:





www.ameteksi.com
Telephone: 865-482-4411

Please see the website for a complete list of the global offices and authorized agents.

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