Princeton Applied Research

VersaSCAN™

Electrochemical Scanning System

- Scanning Electrochemical Microscopy (SECM)
- Scanning Vibrating Electrode Technique (SVET)
- Localized Electrochemical Impedance Spectroscopy (LEIS)
- Scanning Kelvin Probe (SKP)
- Scanning Droplet Cell (SDC)
- Non-Contact Optical Surface Profiling (OSP)

AMETEK

Introducing...

The VersaSCAN is a single platform capable of providing spatial resolution to both electrochemical and materials-based measurements. Traditional electrochemical experiment measure an average response 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 need to investigate localized phenomenon led to the emergence of scanning probe electrochemistry.

By making the measurement at a probe above the surface of the sample, the response is taken from a subset of the sample. A small measurement probe positioned very close to the surface, but non-contact, reduces the sampling volume and provides a high spatial resolution. However, these small responses require superior measurement technology to record the measured parameter. The VersaSCAN integrates capabilities of proven models of Ametek instrumentation, such as the low-current measurement technology of the VersaSTAT and the high dynamic reserve of the Signal Recovery 7230 to extract these data.

The positioning system of the VersaSCAN is based entirely on piezoelectric motors. These motors give long travel (100-mm) and superior resolution (50-nm) in a small footprint.

Different auxiliary pieces interface to the positioning system to provide functionality for several different scanning probe experiments:

- Scanning Electrochemical Microscopy (SECM)
- Scanning Vibrating Electrode Technique (SVET)
- Localized Electrochemical Impedance Spectroscopy (LEIS)
- Scanning Kelvin Probe (SKP)
- Scanning Droplet Cell (SDC)
- Optical Surface Profiler (OSP)

A single scanning platform and software is used for any of these techniques.

Integration of a high-resolution, long-travel positioning system; different auxiliary pieces, such as measurement probes, piezo vibration stages, laser heads; and superior measurements devices such as potentiostats and lock-in amplifiers make the VersaSCAN possible.

...the VersaSCAN

Advantages of the VersaSCAN

Enhanced Technical Features:

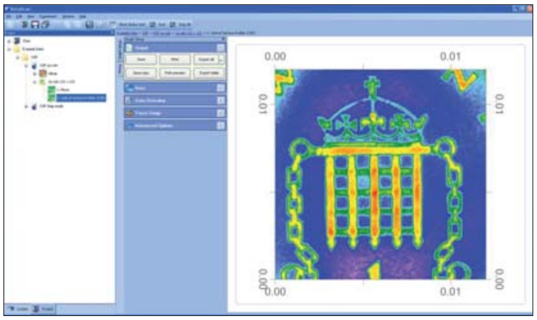
- Single expandable platform capable of SECM, SVET, LEIS, SKP, SDC and OSP experiments
- Superior signal measurement and noise discrimination from integration of VersaSTAT 3/ 4/ 3F Potentiostats and Signal Recovery 7230 Lock-in Amplifier
- Advanced positioning system provides long travel (100mm), high resolution (50nm) and improved repeatability (250nm)
- Vibration-resistant optical base employing both a honey-comb internal design and stiff steel surfaces.
- Ethernet connectivity between devices.

Installation and Training Features:

- Professional on-site installation and training provided, including assembly, verification, demonstration of both hardware and software.

Software Features:

- Preloaded on supplied high-quality laptop.
- Single software platform for all scanning probe techniques.
- Straight-forward configurations with step-by –step guides and easy-to-follow connection diagrams.
- Imbedded ability to rotate data view for an improved graphical presentation.
- Navigation tree design allows for setup of single experiments, building of both simple and complex sequences, and viewing of different data files within the project.
- Ability to export results as images or tables for importation into other analysis or report generating programs.



SECM

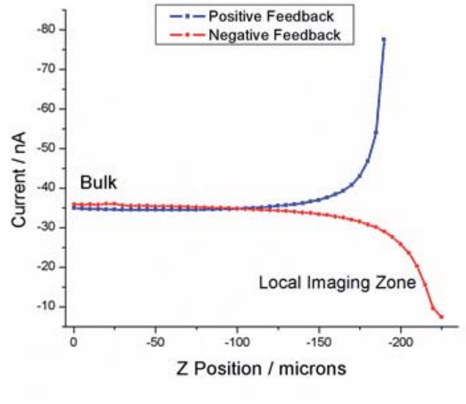
Scanning Electrochemical Microscopy

Introduction

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 activity.

Approach Curves are used as an electrochemical means by which to position the probe in Z sufficiently close to the sample to be in the local imaging zone. Current at the tip is charted as the tip is incremented towards the sample. When the probe is sufficiently close to the sample (a distance of 2-4 times that of the probe diameter) the measured current at the tip transitions from a bulk response to a local response. Over a region of high conductivity, a Nerstain response provides a local current enhanced over that of the bulk current. However, local current is decreased relative to bulk value over areas of insulating nature of the sample as mass-transport is hindered to the tip.

A common experiment in SECM is Generator-Collector Mode. Here one channel of the bipotentiostat polarizes the sample; where the other channel polarizes the tip. Similar to a Rotating – Ring Disk Electrode (RRDE) experiment, one electrode generates an electrochemical reaction, the products of which are subsequently measured at the other electrode. A SECM does this while adding the extra dimension of spatial resolution to the data, and being able to change from Sample Generation – Tip Collection (SG-TC) to Tip Generation –Sample Collection (TG-SC) often by simply changing polarization levels.



Approach Curve experiments using Feedback Mode SECM operation. Gold shows enhanced current; Insulator shows hindered current within the Local Imaging Zone.

Applications

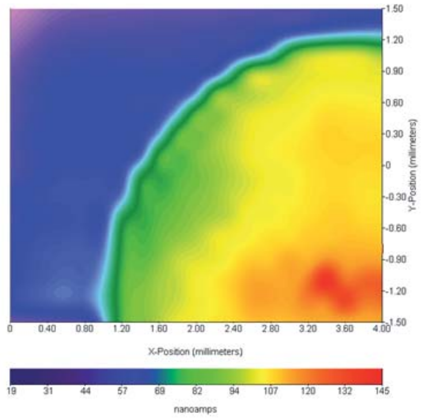
Since the imaging mechanism is electrochemistry, the applications of a SECM are as varied as the applications of electrochemistry itself. Some key fields that have already benefited are biological sensors, reaction kinetics, porous membrane study, fuel cell catalysts, and corrosion mechanisms.

Key Specifications

Several different models of potentiostats from the popular VersaSTAT series can serve as the channels of the bipotentiostat. However, at least one of these channels must be the VersaSTAT 3F as it is capable of “floating ground” operation. This is required as two working electrodes will be in a common cell.

- Compliance Voltage: ±12V
- Polarization Voltage: ±10V
- Current Ranges:

  VersaSTAT 4: 4nA to 1 standard
  VersaSTAT 3F: 4nA to 650 mA standard
  VersaSTAT 3: 200nA to 650mA standard
- Compatible Instrumentation: VersaSTAT- Series of potentiostats. One Channel may be any version VersaSTAT 3/3F/4



SECM Area Scan using Sample Generation – Tip Collection (SG-TC) operation. Gold/Epoxy sample in ferriyanide solution.

SVET

Scanning Vibrating Electrode Technique

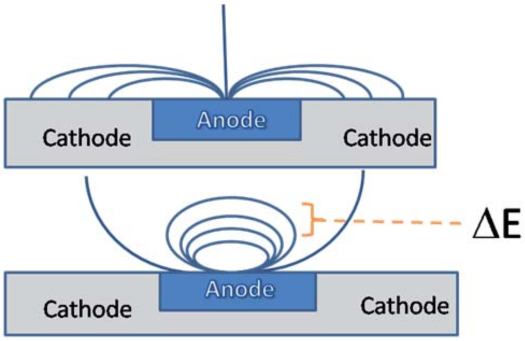
Introduction

The Scanning Vibrating Electrode Technique uses a single wire to measures 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 10s 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 gained 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 recorded and the probe is repositioned. A data map results as voltage versus position are displayed.



Current path and resulting voltage-fields created from local electrochemical reactions on the surface of a sample. Δ E represents the measured value of the SVET experiment .

Applications

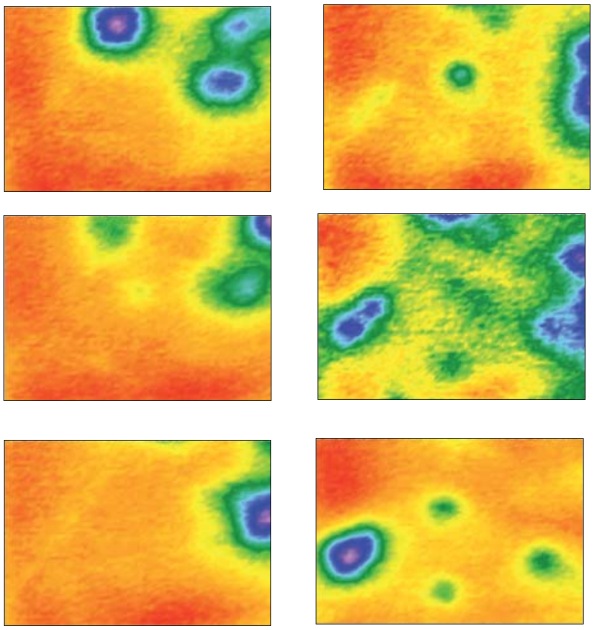
A key application of SVET is to study corrosion process of bare metals. These metals could be galvanic couples or these fields could occur from local non-uniform corrosion events, such as pits or crevices.

Time-lapse experiment series provide the capability to literally 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.

Key Specifications

- Probe Material: Pt/Ir
- Electrometer Range: ±10V
- Electrometer Gain: from 1x to 10,000x in decades
- Application based keys of the 7230:
  - DSP Stability (not analog-based, impervious to temperature drift)
  - High Stability (no fan for failure)
  - Radically better Noise Sensitivity (13 fA/√Hz)
- Piezo Unit: 0-30μ vibration perpendicular to sample
- Compatible Lock-in Amplifier: Signal Recovery 7230



Time-resolved SVET images of the same area of an actively corroding sample taken at different exposure times in electrolyte.

LEIS

Localized Electrochemical Impedance Spectroscopy

Introduction

The VersaSTAT 3F applies an AC voltage to the sample emerged in electrolyte. This “global” voltage generates AC current to flow at the electrode / electrolyte interface. A dual-element probe is positioned in solution close to the surface of the sample. The electrometer measures a differential voltage measure between the two measurement elements as a measure of local voltage-drop in solution. This voltage-drop exists in solution because of current flow from local reactions at the sample, the resistance of the electrolyte and the spatial separation of the dual measurement elements.

The VersaSCAN’s electrometer inputs its measured voltage to the auxiliary differential voltage input available with the VersaSTAT 3F.

Software integration converts the measured local voltage-drop at the probe to local AC current.

The ratio of local measured current to the global applied voltage gives the localized impedance magnitude and phase shift.

Applications

There are two different test methods for the experimentalist to use LEIS to evaluate their samples

A) Chart the local response of a sample from a range of applied AC frequencies in a single location.

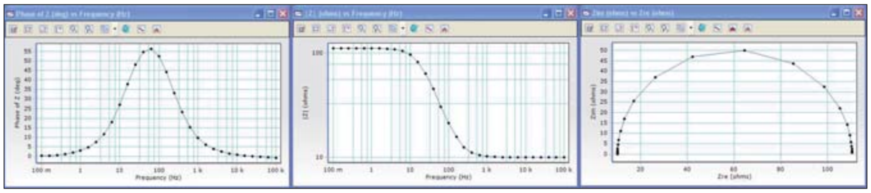
Data can be viewed in either a Bode or Nyquist representation.

B) Create a series of data maps to characterize an AC response as a function of probe position.

Data can be used to create a map, using either Magnitude or Phase as the response.

LEIS provides a spatially resolved impedance measurement that adds value to:

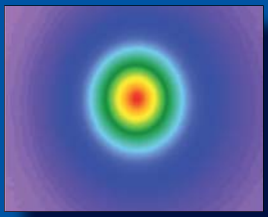
- Inorganic / organic coatings research
- Localized corrosion
- Coating integrity, e.g. delamination, defects, bubbling.
- Variations in coating thickness
- Surface contamination
- Inhibitor studies



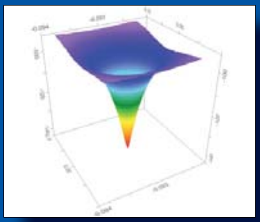
Results of a fixed-position swept-frequency LEIS experiment. Results can be viewed as a bode plot of the phase or magnitude and a Nyquist plot.

Key Specifications

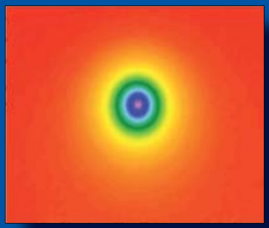
- Probe Material: Pt/Ir pin; Pt ring.
- Electrometer Range: ±10V
- Electrometer Gain: from 1x to 10,000x in decades
- Compatible Potentiostats: VersaSTAT 3F with Differential Aux option
- Differential Aux:
  - Can be single-ended or differential
  - ADC: 16-bits
  - ADC Voltage resolution: 305µV at X1 gain; 61µV at X5 gain; 30.5µV at X10 gain; 6.1µV at X50 gain.
  - Bandwidth ≥ 3 MHz



2-dimensional magnitude



3-dimensional Plot



2-dimensional Phase

Area Scan experiment of LEIS. 200-um gold wire with applied current to simulate local current event, such as a pinhole or pit.

SKP
Scanning Kelvin Probe

Introduction

The Kelvin Probe experiment uses a nondestructive method to determine the relative work function difference between the probe and the sample. Work function describes the energy required to liberate an electron from the surface of a conductor; electrochemists often interpret this as the energy difference from an electrode's Fermi Level, average energy of electrons, and that of vacuum.

A metal microprobe is positioned close to the surface of the sample (on the order of 100-microns). If the microprobe and sample are of different metals, there is an energy difference between their electrons. The microprobe is then electrically shorted to the sample, through internal electronics of the system. As a consequence, one metal forms a positive charge on its surface and the other metal forms a negative charge on its surface. The probe and sample are separated by a dielectric (air), so a capacitor is formed. The probe is then vibrated and "backing potential" or "nulling potential" is then applied sufficient to minimize this capacitance. At the applied voltage that causes the capacitance to go to zero, the original state is achieved. This value is recorded and charted.

Experiments are typically performed in ambient gaseous conditions, but several published examples use humidified environments. The underlying conducting sample can have an organic coating or paint applied.

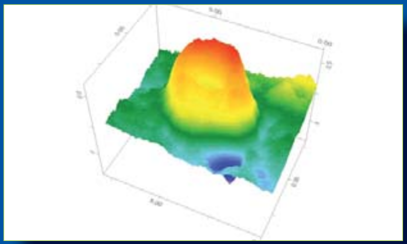
This relative work function can also be correlated to an Ecorr value.

Our SKP is also capable of functioning in Topography Mode. Without changing connections or probe, a reference voltage is applied to the sample. This reference voltage makes the surface of the sample uniform. Change in capacitance is then from a changing plate separation (via equation of a capacitor). This is the probe-to-sample distance.

This information can be used in 2 ways:

Position the probe a known distance from the sample, using a Calibration Coefficient.

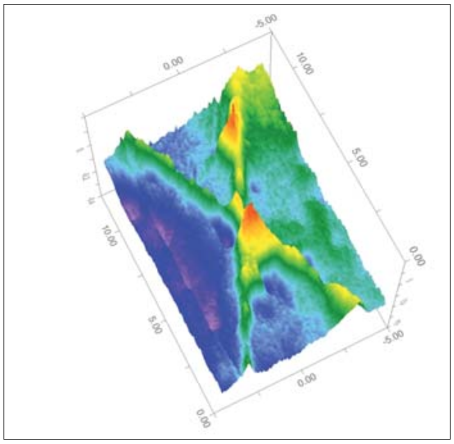
Map topography for further use in Constant-Distance Mode SKP. This is particularly useful in studying welds or other samples of complex topography.



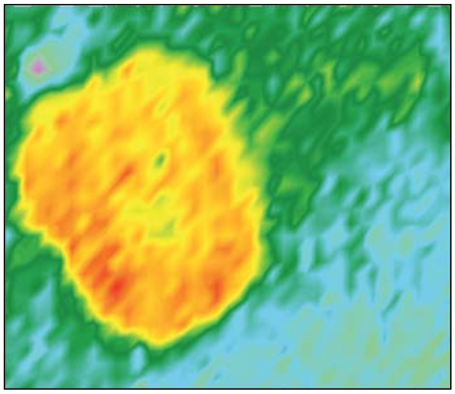
3-dimensional plot of SKP Area Scan data mapping response of a Zinc/Steel surface.

Key Specifications

- Probe Material: Tungsten. Multiple diameters available
- Electrometer Range: ±10V
- Electrometer Gain: from 1x to 10,000x in decades
- Compatible Lock-in Amplifier: Signal Recovery 7230



SKP Area Scan experiment on a metal sample with an organic paint applied and a scribed "X".



2-dimensional plot of SKP Area Scan data mapping response of a Zinc/Steel surface.

SDC

Scanning Droplet Cell

Introduction

Scanning Droplet System (SDC) uses a compact peristaltic pump to force electrolyte through a small diameter tube and into a specifically designed head. This PTFE-based SDC head is machined to allow electrolyte to flow past an installed Reference Electrode and then to a port at the base of the head. When the head is positioned sufficiently close to the sample a droplet forms between the head and sample. Tubing is also connected to an output port of the PTFE head. A second channel of the same peristaltic pump is then used to draw electrolyte past an installed Counter Electrode and out of the system.

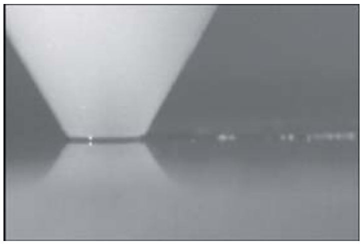
SDC experiments can be configured to either:

- Apply a constant bias (potential, current or open circuit) and increment position of the head creating a data map.
- Apply a static or dynamic electrochemical signal, such as a EIS experiment, a Tafel plot, or a Cyclic Voltammetry experiment as the head is kept in a fixed location.

Since electrochemistry occurs at an electrode/ electrolyte interface, only the portion of the sample that is in contact with the droplet is being measured. This allows experiments to study a small area of a large sample, without cutting the sample and thus limiting edge effects.
When running, the SDC pump creates a flowing droplet. SDC's pump velocity can be tuned to study effects of flow rate.

Key Specifications

- SDC Head Material: PTFE
- Tubing Material: Tygon
- Reference Electrode: Ag/AgCl
- Counter Electrode: Pt Wire
- Compatible Potentiostats: VersaSTAT 3 / 3F / 4



SDC head with its reflection pictured. Note : the droplet of electrolyte exists between this aperture and its reflection.

OSP

Non-contacting Optical Surface Profile

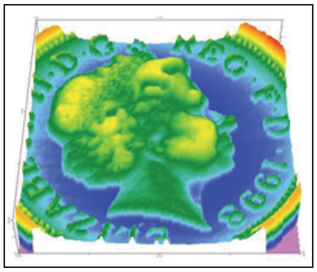
Introduction

The OSP experiment maps topographic changes on a sample surface. This is a laser-based technique.

Map topographic differences to characterize corrosion pits, sensors, etc.

Create a topographic map for integration for other scanning probe technologies in Constant Distance Mode

Use as a highly accurate leveling mechanism before other scanning probe techniques.



OSP results measuring topography of a British coin.

Key Specifications

- Measurement Range: +/- 10mm
- Laser: Class 2, 650nm, 0.95mW
- Repeatability: 0.025µ.
- Spot Size: 50µ at reference distance of 50mm.

VersaSCAN options

VersaSCAN L-Cell

- Screws into optical table of VersaSCAN
- Approximately 1 Liter in volume
- Level adjustment mechanism
- Accepts large flat samples and 32mm diameter mounted samples
- Recommended for all techniques, particularly LEIS, SVET, SKP, SDC, OSP

VersaSCAN mL-Cell

- Screws into optical table of VersaSCAN
- Approximately 7 mL in volume
- Level adjustment mechanism
- Accepts a range of samples including 32mm diameter mounted samples and non-standard samples
- Specifically engineered for low-volume SECM applications.

VersaCAM

- Camera:

  Color
  Number of Pixels: 795 (H) x 596 (V)
  Minimum illumination 0.02 lx. F1.2
  Power: 12V DC +/- 10%
  CS-mount or C-mount with provided adapter.
- Lens:

  C-Mount
  Manual focus.
- Display:

  8 inch color TFT display
  PAL & NTSC auto selection
  640 x 480 (307,200 pixels) screen resolution

specifications

Dimensions

Scanning Head:

300mm W x 470mm H x 600mm D
66.3lbs; 30kg

Control Unit (each):

360mm W x 120mm H x 300mm D
9.3lbs; 4.3kg

Potentiostat:

421mm W x 89mm H x 387mm D
10lbs; 4.5kg

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