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Review—The Use of Localized Electrochemical Techniques for Corrosion Studies

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While global electrochemical techniques, such as Electrochemical Impedance Spectroscopy (EIS), have been utilized in corrosion and coatings research for over forty years, the refinement of those techniques into localized methods is a more recent development. In this review, in honor of Hugh Isaacs, the authors have focused on developments in localized methods of importance to corrosion research. Receiving special attention in the review are the following methods: Scanning Vibrating Electrode Technique (SVET), Localized Electrochemical Impedance Spectroscopy (LEIS), Scanning Electrochemical Microscopy (SECM), Scanning Kelvin Probe (SKP), Scanning Ion-Selective Electrode Technique (SIET), and Scanning Droplet Cell (SDC) Technique. For each method, a summary of the method along with several examples of its use in the area of corrosion and coatings are provided. Additionally, synergies with electro-microimaging techniques are discussed which highlights the often complex experimental designs required to probe the mechanisms of corrosion.

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The translation of global electrochemical techniques into local resolutions is an inherently complex process. In addition to increased computer requirements there is significant increase to the mechanical instrumentation such as in the positioning capabilities of a probe, microscope, or micro-electrochemical cell; often with sub-micron resolution required. Perhaps the increased specialization of the instrumentation is the reason for the first development and propagation of the many global techniques such as Electrochemical Impedance Spectroscopy (EIS), Polarization Resistance (Rp), and Tafel methods. However, in the world of corrosion research, very rarely (if at all) is the corrosion process considered to be a uniform process on a macro-scale. For this exact reason, there has been a push to “focus” on the local processes occurring during corrosion. Several localized techniques have been developed over last few decades which have found significant use in the corrosion area for the mechanistic understanding of corrosion processes at the local level. Table I lists these localized methods.

This article belongs to the special issue in the memory of Dr. Hugh Isaacs. He was a pioneer who carried out a significant amount of research on the early development of microelectrodes and localized corrosion which form the ground-work of the localized electrochemical techniques which are used today. In 1972 he used a scanning reference electrode technique for counting the active pits on corroding 304 stainless steel.¹ Thereafter diffusion in the case of localized corrosion was studied by using wire electrodes which were placed in an inert support surrounded by various corrosive environments.^{2,3} A vibrating probe electrode was used to study current flows and potential response to applied current on passive stainless steel at local corrosion sites.⁴ Also an in situ scanning vibrating electrode technique was used for looking at the initiation of stress corrosion cracking.⁵ He and his colleagues also pioneered the development of LEIS for mapping local electrochemistry.⁶ He has extensively employed in situ X-ray absorption near edge spectroscopy (XANES) for studying passivity on metal substrates as well as for the characterization of chromate conversion coated substrates.^{7,8} He also contributed to the development of ion-selective micro-tipped electrode (ISME) for use in the SECM technique for the detection of Mg²⁺ ions.⁹

Certainly without the contributions of Dr. Hugh Isaacs, the intellectual landscape in the area of localized electrochemical techniques for corrosion research would be much less rich. The early work done by Dr. Hugh Isaacs paved the way for the development of localized

methods and their application for corrosion research. In this review paper we focus on the most relevant and widely used techniques for corrosion research. For each technique, we discuss the theory along with how it works and then proceed to explain how it is being used for corrosion research. While providing examples of use in corrosion research we are focusing on the most significant applications and recent approaches. Wherever necessary, we are adding information such as resolution, advantages, disadvantages, and specific uses for the particular technique throughout the paper. Along with information in the text of the paper, advantages and disadvantages of discussed localized techniques are presented in Table II. Keeping into consideration the vast literature published on each of these techniques,¹⁰ an attempt has been made to provide a concise account of recent developments about localized electrochemical techniques.

Scanning Vibrating Electrochemical Technique (SVET)

Technique details.—Due to its ability to provide a visualization of local cathodic and anodic reactions, SVET is finding a multitude of uses in the study of corrosion and related topics. This in-situ, local technique utilizes a vibrating conductive probe (Figure 1) which measures the potential difference in an electrolyte that is in contact with a corroding metal (between probe and substrate). This is accomplished by vibrating the probe on multiple axes (could be vibrated on one axis depending on measurement and instrument type) and referencing a probe far from the sample surface. The potential difference exists as there is a small electric field within the electrolyte solution due to the ion flow in solution and electron flow in the corroding metal as shown in Figure 2.

Measuring the potential difference and knowing the amplitude of vibration along with the resistivity of the solution leaves a simplistic equation for determining the current at that location. Where I is the current, ΔE is the voltage difference, d is the amplitude of vibration, and ρ is the resistivity of the electrolyte. The process of obtaining the current density magnitude is then repeated in a predetermined grid to receive a plot of the current density over a selected surface of the sample. A full review of the theory and mathematics is beyond the scope of this review paper, but the authors encourage interested readers to review the papers by Dogikh et al. and Rossi et al. for more detailed discussions.^{11,12}

$$I = -(1/\rho) (\Delta E/2d) \quad [1]$$

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Table I. A brief summary of the techniques, properties measured, and uses.

Technique	Measurement	Example of Uses
Scanning Vibrating Electrode Technique (SVET)	Potential Difference/Current Density	Location of oxidation and reduction half-cells and corrosion rate.
Localized EIS (LEIS)	Local Capacitance and Resistance	Local variations in EIS and related variables such as CPE
Scanning Electrochemical Microscopy (SECM)	Current	Localized electrochemical activity, O ₂ concentration, etc.
Scanning Kelvin Probe (SKP)	Work Function	Delamination studies, impact of intermetallic particles on corrosion
Scanning Ion-Selective Electrode Technique	Local pH, ion concentration	Corrosion inhibitor mechanisms, ion migration
Scanning Droplet Cell (SDC) Technique	Potential, Current	Alloying element impact on corrosion

Table II. Localized Electrochemical Techniques: Advantages and Disadvantages (more information is provided in the text of the paper).

Technique	Advantages	Disadvantages
Scanning Vibrating Electrode Technique (SVET)	Real time mechanistic information, 2D-3D data presentation, easy to set up, easily used with other techniques such as SIET	Time and sample size tradeoff, could be slow, cannot use high conductivity electrolyte and high amplitude of vibration, open to air so loss of electrolyte is a concern
Localized EIS (LEIS)	High sensitivity (1 nV), provides local impedance which cannot be obtained by any other method, good for insulated substrates (such as coating on substrate)	Stray inductance, could be slow
Scanning Electrochemical Microscopy (SECM)	Several modes of operation, can be combined with other techniques	Sometimes needs a redox active mediator, needs a bipotentiostat
Scanning Kelvin Probe (SKP)	No need of an electrolyte, short experiments	Low resolution of SKP but SKPFM could have high resolution, need of probe calibration
Scanning Ion-Selective Electrode Technique	Can be combined with SVET, easy way to measure ion concentration	Fouling and damage to the ion selective electrode, resolution
Scanning Droplet Cell (SDC) Technique	Minimum electrolyte contact with surface, can do all the electrochemistry technique with simple set up	Droplet drag, surface energy issues

Data can be represented via multiple graphical views. Examples of 2D and 3D representations are shown on the next page in Figure 3.¹³ Oftentimes the data is presented along with an image showing the concurrent physical damage/corrosion that occurred during the experiment.^{14,15}

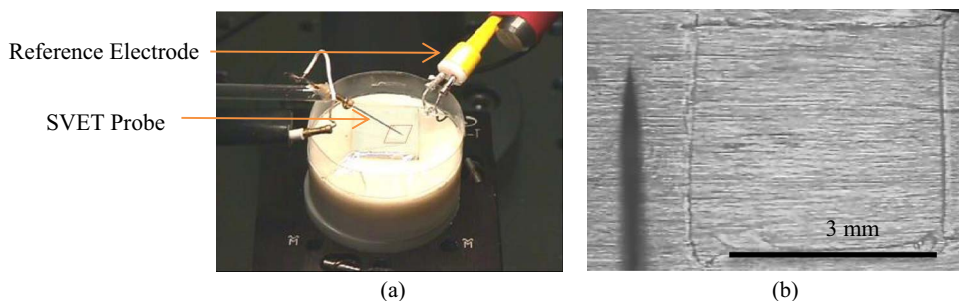
There are a few important experimental limitations for the use of SVET in corrosion studies. Due to the time required to raster the probe in a grid formation, along with the time for data acquisition at each stop in the matrix, there is a tradeoff between the size of the sample that is reasonable to measure along with the resolution of the grid used for that area. Additional complications can arise if the sample is not completely flat or isn't leveled properly in comparison the scanning probe. Also of concern for longer duration measurements, the evaporation of the electrolyte can cause artifacts, one of which is the loss of in-focus imaging due to the change in the focal length as the electrolyte height decreases. Finally, to maximize the potential difference in the electrolyte, dilute electrolyte solutions are preferred for this technique.

In addition to providing the ability to detect the potential difference, there is a benefit to the vibrating action of the probe as it can provide local mixing in the electrolyte, thus limiting concentration gradients. However, care must be taken to avoid larger amplitude vibrations as the increase in mixing can impact diffusion controlled corrosion reactions, such as the oxygen reduction reaction.^{11,16}

For detailed information in the form of a recent (2017) review article, please see "Review: On the Application of the Scanning Vibrating Electrode Technique (SVET) to Corrosion Research." In the review, Bastos et al., provides an in-depth review of both the mechanics, theory, and uses of the technique.¹³

Examples of Use in Corrosion Research

In recent years, SVET has been used to better understand the behavior of uncoated metals exposed to corrosive electrolytes. Mena et al. used the technique to probe the localized distributions of anodic and cathodic sites for zinc exposed to diluted artificial ocean water.

**Figure 1.** Vibrating probe and SVET electrochemical cell, a) photograph of SVET set up and b) photograph of exposed sample to SVET measurement.

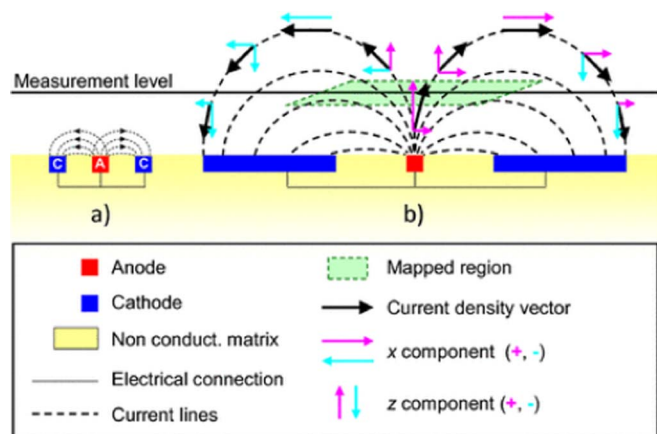


Figure 2. Electrochemical phenomenon occurring during corrosion that can be determined by SVET, a) area with low current activity and b) area with high current activity.¹³ Reprinted from the *Journal of the Electrochemical Society*.

Mena et al. found that longer immersion times were required to resolve the anodic and cathodic sites in comparison to the background noise that was observed during their measurement.¹⁷ Williams et al. studied the localized corrosion processes for magnesium alloy AZ31 when exposed to a 5% w/v chloride containing electrolyte. With SVET, the authors were able to determine that several advancing, prominent anodic sites were responsible for the darkened areas. These mobile anodic sites were coupled with cathodic regions that were also in the corroded area. Areas that were resistant to the darkening, were void of cathodic and anodic sites and were later determined to be electrochemically inert in comparison to the corroded area.¹⁸

One interesting application was reported by Manhabosco et al. as they used SVET to verify the increased corrosion rate of laser marking on M340 martensitic stainless steel. M340 is often used in biomedical applications and requires laser marking for tracking purposes. The SVET results indicated a passivity of the unmarked M340 in 0.1 M naturally aerated NaCl, however, the laser marked areas show active dissolution via SVET due to Cr-depleted regions.¹⁹

The understanding of galvanic couples has also received attention in the area of SVET. Li et al. studied the galvanic corrosion of an Al-Mg₂Si couple. The couple was exposed to aerated 0.01 M NaCl at a variety of pHs. It was found that bulk Mg₂Si is anodic to pure Al in acidic solutions. With longer immersion times, the anodic activity

of Mg₂Si decreases with subsequent corrosion initiation on the Al metal as shown in Figure 4. The work also highlights the complexity of galvanic couples at different pH.²⁰

Another galvanic couple, this time between Al-Cu-Mg was studied by Snihirova et al. For this work, wires of Cu and Mg were embedded in a pure Al matrix. The couple was designed to emulate the S-phase of AA2024-T3. The SVET results were coupled with pH and oxygen distribution measurements to determine that cathodic reactions could occur both on the Cu and the Mg. While the Mg cathodic reactions were not found via SVET, the pH and oxygen depletion clearly indicated cathodic reactions were, indeed, occurring. The work also investigated the use of corrosion inhibitors in-situ during the SVET measurements.²¹ Thebault et al. used the technique to study the mechanism of protection at cut edges on galvanized steel.²² In this real-world galvanic couple example, SVET was able to determine three distinct kinetic regions, an anodic area over the zinc surface, a corresponding cathodic area over the steel, and a third region comprised of the inhibition of oxygen reduction. Similar application for characterizing cut edge corrosion was studied by Ogle et al.²³

SVET has also been found useful in the area of corrosion inhibitors and inhibition. Multiple papers have focused on the use of the technique to determine in the impact of corrosion inhibitors. Borisova et al., used mesoporous silica nanoparticles filled with benzotriazole and found pH triggered self-healing and anticorrosive properties via SVET.²⁴ In 2007, Zheludkevich et al. utilized SVET to probe a self-healing sol-gel coating containing an organic inhibitor. The results clearly showed that when the sol-gel was doped with the inhibitor there was a self-healing at a defect site, as indicated by a decrease in the anodic current over time. In comparison, the same sol-gel without the inhibitor saw stable anodic reactions over one day of immersion time in 0.5M NaCl.²⁵ That same year, Zheludkevich et al. presented results showing similar self-healing behavior for work based upon nanocontainers filled with corrosion inhibitors.²⁶

Other teams have used SVET to study the self-healing or 'smart' response coatings, most focusing on the magnitude of the current in a defect area over time as an indicator of possible self-healing and/or responsive corrosion inhibition. Among some notable examples, Taryba et al., studied layered double hydroxide (LDH) nanocontainers and found that the coatings filled with the LDH nanocontainers displayed significant corrosion inhibition.²⁷ Tedim et al., also studied LDH, this work focused on an LDH conversion coating formed electrochemically. The authors found the LDH thin layer was an effective corrosion inhibitor for long periods of time, with times of up to 1 month studied. The best performance was observed when the LDH was intercalated with vanadates.²⁸ Yan et al. studied an aluminum flake coated with an

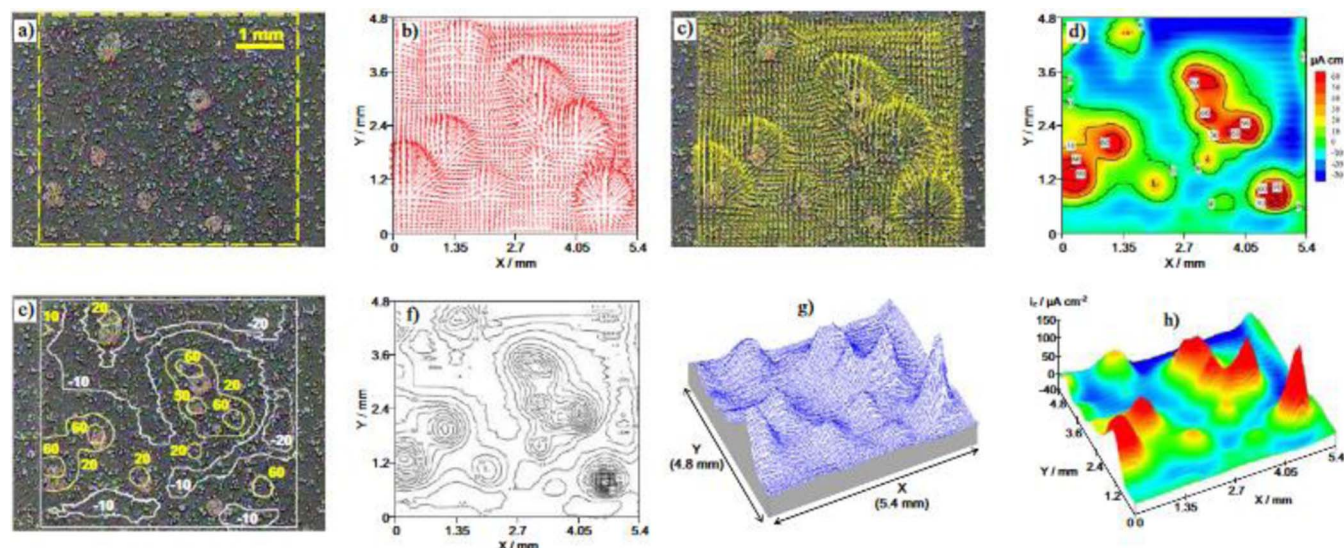


Figure 3. The various ways to represent SVET data.¹³ Reprinted from the *Journal of the Electrochemical Society*.

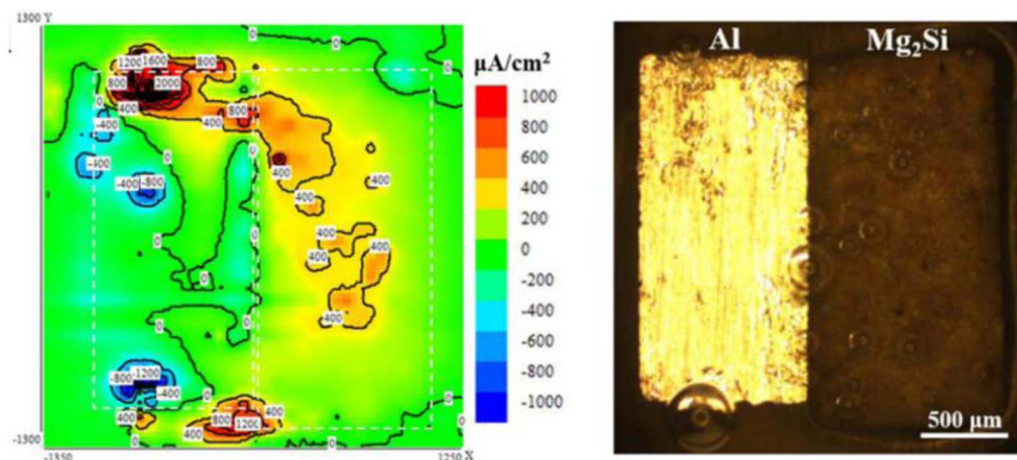


Figure 4. Current density distribution (left) and optical image (right) for galvanic couple after 22 hours of immersion in 0.01 M NaCl (pH = 2).²⁰ Reprinted from the *Journal of the Electrochemical Society*.

electroactive conducting polymer for corrosion inhibition. They found via SVET that the corrosion inhibition was dependent on the dopant choice, with some dopants showing no or limited corrosion inhibition, and others, such as those doped with molybdate or vanadate species, displaying significant inhibition.²⁹

Recent papers from Coelho et al., have focused on benzotriazole and cerium chloride as potential corrosion inhibitors, both papers studied the inhibitors alone or in combination. The initial paper found a synergistic effect via SVET, however when the work was translated from the model system to full alloy, limited protection was observed.^{30,31} These results highlight one of the challenges of localized electrochemical methods, as it is possible for results from model systems to not translate to the more complicated real-world specimens.

Finally, while there has been significant attention given to new inhibitors, that does not mean that SVET has not been used to study the more traditional inhibitors, such as the use of chromates and phosphates. He et al., used SVET to study the mechanism of inhibition of hexavalent chromate containing epoxy primer on both steel and aluminum in 2000.³² Bastos et al., used SVET to study chromate and phosphate extracts in contact with iron substrates. Both teams saw the bene-

ficial properties of chromate. However, it was found that the zinc phosphate provided no short-term corrosion inhibition in 0.1 M NaCl.³³

Localized Electrochemical Impedance Spectroscopy (LEIS)

While Electrochemical Impedance Spectroscopy (EIS) has been widely used in the last few decades, the localized application of the technique is a more recent development, introduced by Hugh Isaacs in 1992.⁶ In LEIS, a global voltage is applied similar to the aforementioned global EIS method; however, a local potential difference is measured at a moveable probe or dual-probe configuration. This potential difference can be used to calculate the local current.

The sensitivity of most modern LEIS instruments is approximately 1 nV. The resolution of the LEIS technique is stated to be approximately 30–40 μm , with this resolution dependent on the size of the probe and/or the spacing of the probes (if dual-probe used).³⁴ Work has been done by Abreu et al. to understand the impact of the probe size on LEIS measurements.³⁵ In their work, it was determined that with small probes (tens of μm or less) there tends to be a high frequency inductive behavior due to stray capacitance between the two wires

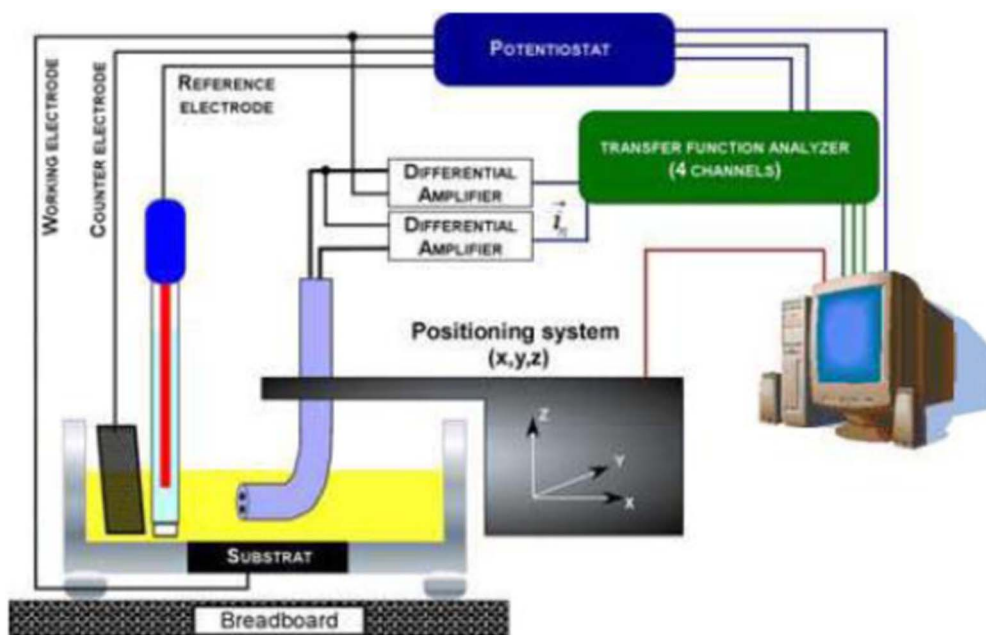


Figure 5. A schematic of one iteration of LEIS.³⁸ Reprinted from *ECS Meeting Abstracts*.

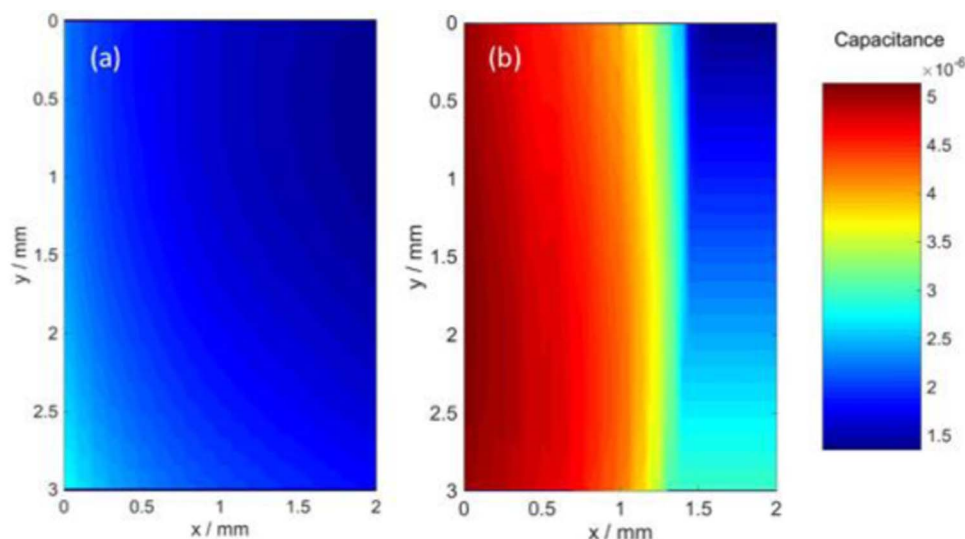


Figure 6. 2D LEIS of Steel under mechanical stress in borate solution.³⁹ Reprinted from the *Journal of the Electrochemical Society*.

of the probe. The authors suggest multiple approaches to reduce this inductive artifact, including reducing the electrolyte resistance and modifications to the experimental approach. Other researchers have utilized the SVET electrochemical setup to refine the resolution.³⁶ While even others have used the micro-capillary setup to localize the area under measurement.³⁷ A schematic of a standard LEIS setup is provided in Figure 5.³⁸

There are two primary variations to this technique. The first is where a fixed frequency potential perturbation is used while the probe tip is moved over the sample in a grid-like fashion while in electrolyte. Typically, this method is used to determine any interesting phenomena, such as a low impedance defect. When an area of interest has been identified, the second variation of the experiment can be performed where the probe can be placed above that area and complete impedance spectra over some frequency range can be acquired. Once the data is acquired, the processing and graphing are similar to EIS however 3D graphs are often used to display the location dependent information obtained using the LEIS technique. This can be done either by a 3D graph or color gradient 2D representation as shown below in Figures 6 and 7.^{39,40}

Examples of Use in Corrosion Research

LEIS has provided the opportunity to further probe the global EIS results on the localized level. In global EIS results, often the capaci-

tances determined are not ideal capacitances and, as such, are modeled by constant phase elements (CPE). For many years, the reason for this diversion from ideal behavior has been hypothesized to be due to distribution of capacitances across the area under measurement or to a frequency dependence of the capacitance. Jorcin et al. used LEIS to investigate the occurrence of CPE for both AZ91 magnesium alloy and pure aluminum in the presence of 0.1 M (EIS) or 10^{-3} M (LEIS) Na_2SO_4 electrolyte. Different phenomena were responsible for the CPE for the magnesium alloy and pure aluminum. AZ91 was found to have a 2D distribution of high-frequency resistance. For the pure aluminum, there was a combination of 2D and 3D distributions that caused the CPE behavior.⁴¹

Galicía et al. also studied AZ91, and pure magnesium, via LEIS and EIS in the presence of dilute Na_2SO_4 . Due to the use of LEIS, the authors were able to determine that the corrosion of both the β -phase and α -phase had the same mechanism that was controlled by the dissolution of Mg. The local technique was also able to provide information about local kinetics, leading to the determination that the dissolution of the β -phase was slower than the α -phase.⁴²

Other research groups have used LEIS to study galvanic corrosion. Mouanga et al. used the localized method to study the galvanic interactions between zinc and carbon steel when exposed to a dilute NaCl solution. The current distribution was higher at the interface between the zinc and carbon steel. This corresponds to a higher corrosion rate of the zinc closer to the steel. Differences were observed when zinc was

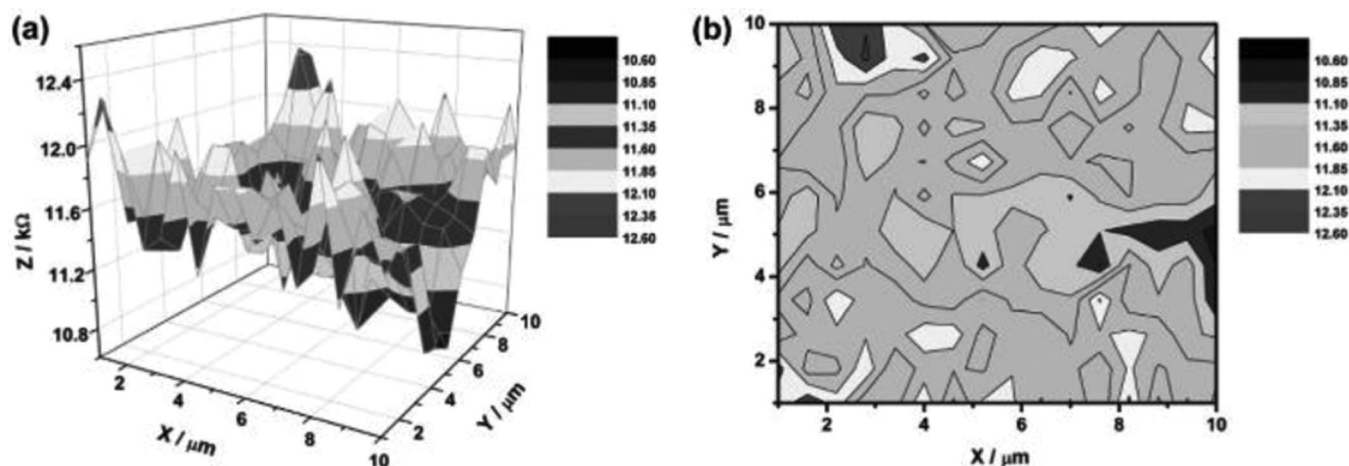


Figure 7. 3D and 2D LESI map of a Ti/Pd-Sb-SnO₂(M) electrode.⁴⁰ Reprinted from the *Journal of the Electrochemical Society*.

coupled to steel versus zinc that was polarized at an identical potential. The authors suggest that the results indicate that researchers must take care when using LEIS to study galvanic corrosion mechanisms.⁴³

Burczyk and Darowicki used LEIS to study both zinc/copper and cadmium/copper galvanic couples.⁴⁴ In the research, a modification to the standard LEIS measurement was used; specifically their experimental method allowed for measurements at a non-steady state. The technique was referred to as dynamic LEIS (DLEIS). To expedite the measurements, multiple frequencies were used concurrently. The authors found that the DLEIS results validated the other galvanic coupling experimental results.

LEIS has found applicability in the study of the delamination of coatings, as shown by Jorcin et al.⁴⁵ In their paper, the use of LEIS to study epoxy-vinyl coated steel in 0.5 M NaCl is discussed. The worked focused on the delamination or undercutting that is often observed when scribed panels are placed into accelerated corrosion cabinets. The delamination was observable by a decrease in impedance attributed to the loss of adherence and failure of the organic coating.

Studies into the corrosion protection provided by functional and smart coatings have also utilized LEIS. Montemor provides a nice review of recent results into such work.⁴⁶ In the paper, the author states that when studying such materials, that spatially-resolved techniques are quite powerful. LEIS has proved to be extremely useful when studying corrosion at coating defects as well as the self-healing mechanism in the new functional coating systems. Another example of such work, Barranco et al., used LEIS to study the corrosion protection provided to mild steel by a sol-gel pretreatment. For their work, a mini-cell system was used to facilitate the acquisition of the LEIS spectra, as shown in Figure 8.⁴⁷

Scanning Electrochemical Microscopy (SECM)

Technique details.—Scanning electrochemical microscope (SECM) utilizes an ultramicroelectrode probe of typically micrometer dimensions held above a substrate immersed in a solution, often with a redox active mediator added to the electrolyte solution. SECM has multiple operational modes, a few of the more commonly used modes are listed below. Feedback and generation/collection modes were the first modes developed, with expanding applications of SECM, more modes have been developed in recent years.^{48,49}

- Substrate Generation/Tip Collection (SG/TC)
- Tip Generation/Substrate Collection (TG/SC)
- Steady-State, diffusion limited behavior in bulk solution
- Feedback mode over inert or insulating substrate (Negative Feedback)

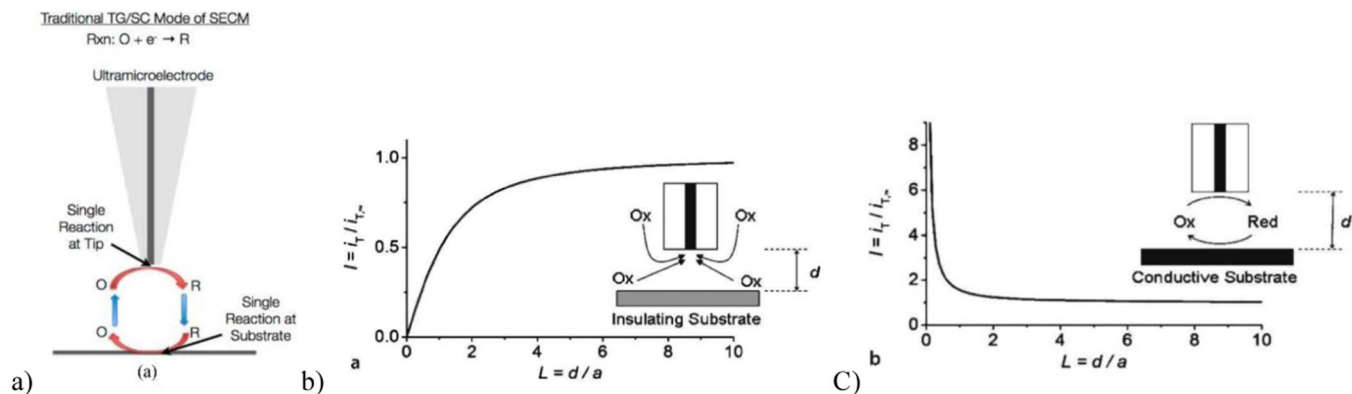


Figure 9. a) A schematic of the TG/SC mode of SECM. Reprinted (adapted) with permission from K.C. Leonard, A.J. Bard, The Study of Multireactional Electrochemical Interfaces via a Tip Generation/Substrate Collection Mode of Scanning Electrochemical Microscopy: The Hydrogen Evolution Reaction for Mn in Acidic Solution, *J. Am. Chem. Soc.* 135 (2013) 15890–15896). Copyright (2013) American Chemical Society,⁵¹ b) negative feedback over insulating surface, and c) positive feedback for conductive surface.⁵⁰ Reprinted from the *Journal of the Electrochemical Society*.

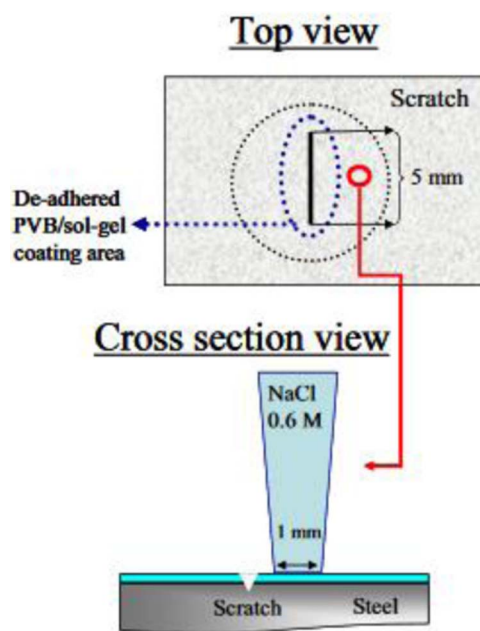


Figure 8. Schematic of the location of an electrochemical mini-cell used to acquire LEIS near a defect area.⁴⁷ Reprinted from *ECS Transactions*.

- Feedback mode over a conducting substrate (Positive Feedback)
- Redox Competition (RC)

An example of the TG/SC mode is shown below in Figure 9. When using a generator/collection mode, the probe tip is typically maintained at a distance to the sample of approximately ten probe tip radii or less. Both the substrate and tip current can be controlled and monitored. For the feedback modes, the nature of the sample becomes significant, with an insulating sample showing negative feedback, while conductive samples typically will behave in a positive feedback mode. Redox competition mode entails having the same, competing reaction occurring at the probe and substrate surface.⁵⁰

Similar to the other localized electrochemical methods mentioned in this review, a 3D micropositioner is used to position the ultramicroelectrode, allowing for spatially resolved electrochemical data to be acquired, as shown in Figure 10.⁹ Movement of the probe in the x or y direction provides information related to the electrochemical activity and/or the topography of the substrate, while moving the probe toward the substrate in the z direction yields information on electron transfer kinetics at the substrate surface.

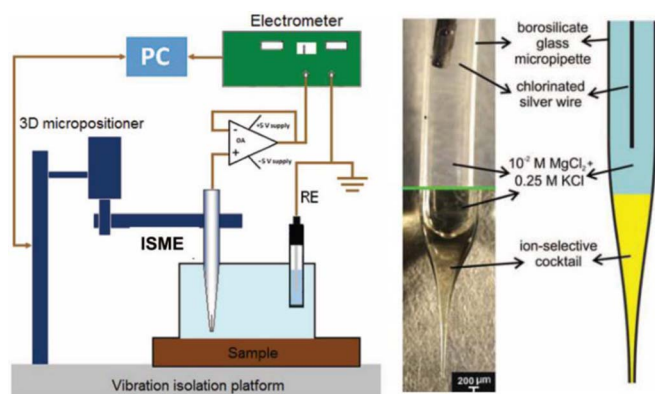


Figure 10. Sketch of the main components for SECM (left) and an example of an ion-selective electrode (right) from Ref. 9. Reprinted from the *Journal of the Electrochemical Society*.

Somewhat unique to SECM is the use of a bipotentiostat, providing independent control and sensing for both the substrate and the ultramicroelectrode. This, along with the multiple available modes of operation and use and selection of a redox active mediator, means that the proper design of a SECM experiment is not trivial.⁴⁸ There are multiple, comprehensive reviews on the technique, owing to its use in many fields of study and complexity of use^{48,52,53} including very interesting book chapter.⁵⁴ There is also a 2010 review on the technique's use in the area of corrosion research.⁵⁵ A more recent 2017 review focused on the use of SECM in corrosion research is also available.⁵⁶ There are also multiple reports on the applications of SECM for corrosion studies.^{57,58}

Examples of Use in Corrosion Research

There are many recent examples of the use of SECM in the area of corrosion, perhaps this plethora of papers is due to the many modes available to the researchers. Importantly, there is a significant amount of papers focused on the technique itself, often with the goal of improving resolution or expanding the applicability of SECM. One such paper from Izquierdo et al., and was focused on the combined use of SECM with atomic force microscopy (AFM).⁵⁹ The work was focused on minimizing the impact of topological changes that occur during corrosion processes, which can impact the recorded current in traditional SECM experiments. The authors were able to use the AFM-SECM method to successfully determine the surface corrosion process for pure copper. Important information was obtained regarding the corrosion product/patinas and pit formations. An alternative approach to non-flat surfaces was studied by Alpuche-Aviles and Wipf who used impedance feedback to control the tip to substrate distance.⁶⁰ In their work, a high-frequency ac current was resolved using a RC filter, which allowed for simultaneous impedance data during a collection/generation experiment.

Kiss et al. studied the effect of the electric field during potentiometric SECM measurements.⁶¹ The authors were able to determine that a strong electric field, such as those observed around galvanic couples, can cause experimental artifacts. In their work, the example of a magnesium/aluminum AZ63 alloy coupled to iron was studied. These artifacts can either cause a under or overestimation of ion activity. It was suggested that this artifact can be minimized by placing the reference and probe in close proximity. An alternative suggestion was of an electric switch between the galvanic couple to allow for disruptions between the galvanic interaction between the dissimilar metals.

In 2016 and 2017, Filotas et al., developed a dual-electrode probe to perform amperometric/potentiometric measurements on corroding galvanic pairs. In one embodiment of their work, antimony and platinum micro-electrodes were fabricated to perform quasi-simultaneous combined measurements focused on chemical detection and pH. It

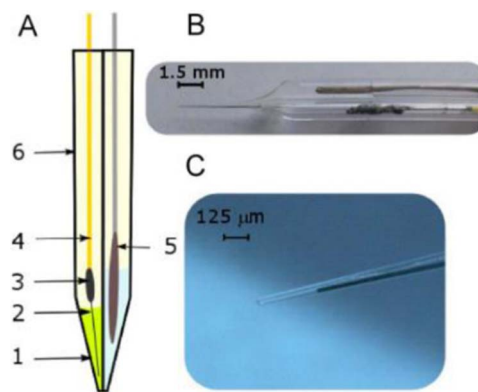


Figure 11. Dual probe design from Filotas et al.⁶⁵ Reprinted from the *Journal of the Electrochemical Society*.

was found that the dual-probe configuration eliminated the issues of replacing probes to switch between amperometric and pH measurements, significantly improving the correlation between the two measurements.^{62–64} In another study, a modification of the dual-probe was found to minimize electric field effects during investigations of galvanic couples during SECM measurements.⁶⁵ An example of the dual-probe is shown below in Figure 11.

Other groups have used SECM to study the localized corrosion phenomena. Ye et al., used submicron SECM probes to study the pitting corrosion of 316L stainless steel in a 0.1M NaCl solution with 1.0 mM ferrocenemethanol.⁶⁶ It was determined that the submicron probe was successful in the pitting investigation and that the small size of the probe led to an improvement in the spatial resolution of the resulting data maps. Kong et al. also studied pitting corrosion, however on Cu-Ni-Zn ternary alloys in 0.5 M NaCl adjusted with a borate buffer to a pH of 9.⁶⁷ The SECM results indicate there was a uniform stable surface current (2.2 nA) in the passive stage, once pitting commenced, there were local maxima approaching 3 nA. The authors show the importance of using multiple electrochemical methods in the paper, and draw more conclusion from the use of potentiodynamic and potentiostatic electrochemical techniques in conjunction with high resolution microscopy techniques.

Hydrogen evaluation from cathodic corrosion reactions has also been studied. Dauphin-Ducharme et al. monitored hydrogen fluxes over corroding Magnesium Alloy AM50 via SECM in SG/TC mode.⁶⁸ Mena-Morcillo et al., used SECM to study the localized corrosion of magnesium alloy AZ31B in simulated body fluid (SBF).⁶⁹ In their work, hydrogen evolution from the magnesium surface was quantified during immersion in the SBF. Hydrogen evolution was found at cathodic sites on the Al-Mn phases. Results are shown below in Figure 12.

SECM has been found to be valuable in the study of corrosion inhibition. Souto et al. used the technique to study the protection provided to steel by a polyurethane barrier coating (dry film thickness was $\sim 60 \mu m$).⁷⁰ The coated specimens were placed in constant immersion in a 0.1 M KCl or K_2SO_4 solution and removed periodically for SECM characterization. A 0.5 M ferrocenemethanol solution was added to the storage constant immersion electrolyte for acquisition of SECM. The authors also performed some experiments without the ferrocenemethanol mediator, in those cases dissolved oxygen was detected. The authors state that early stages of blister formation have been detected by using SECM; however, there is uncertainty if all nucleated blisters develop into a macroscopic failure. Carbonell et al., studied a variety of sol-gel coatings applied to AA 2024-T3; all were exposed to 5mM NaCl with 0.5 mM ferrocenemethanol solution.⁷¹ In this work, SECM was shown to be useful in providing the mechanism of inhibition of the Na-(diethyl(ditiocarbamate)) (DDTC). An increase in electrochemical activity of the coating containing DDTC was observed after the application of a cathodic polarization.

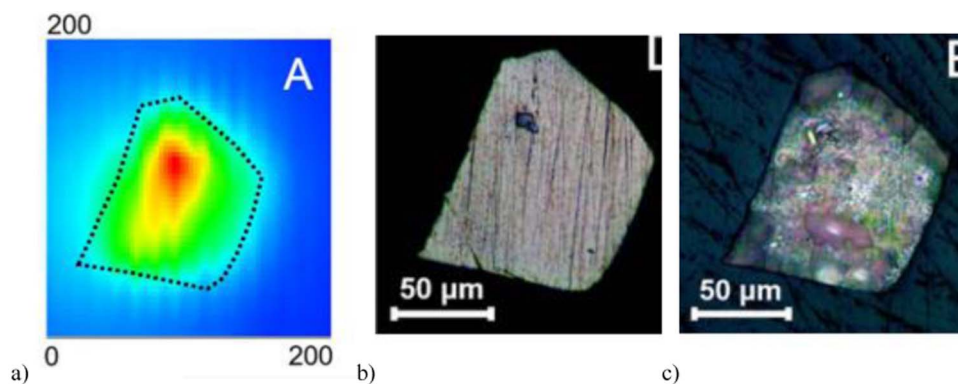


Figure 12. a) Probe (tip) current after 1 hour immersion in SBF, b) optical image prior to immersion, and c) optical image after experiment complete.⁶⁹ Reprinted from the *Journal of the Electrochemical Society*.

Passivity has been studied by Torbati-Sarraf and Poursaei.⁷² In their work, carbon steel exposed to simulated concrete pore solution was examined via SECM. Z-approach curves after different lengths of time of exposure to the simulated concrete pore solution were obtained to ultimately determine the kinetics of passivation layer formation. Yanagisawa et al. studied the passivity of dual-phase carbon steel in a buffer solution via TG/SC mode. Pure ferritic, pure martensitic, and dual-phase carbon steel were studied.⁷³ Prior to collecting the tip current image, 0.7 V (vs SHE) for 3600 seconds was applied to the substrate. SECM results indicate that the dual-phase displayed a higher conductivity through the passive film on the martensitic phase than the ferritic phase areas. The impact of selected laser melted (SLM) Stainless steel 304L was studied by Schaller et al. also in feedback mode. SECM results indicated the loss of corrosion resistance of the SLM 304L.⁷⁴ Lee et al. probed the effect of hydrogen sulfide ions on 316L stainless steel passivity.⁷⁵ It was found that hydrogen sulfide ion caused instability in the typical passivity of the 316L.

Similar SECM techniques, such as feedback mode, to those employed in the study of passivity have been used to study corrosion product formation. Dauphin-Ducharme et al. studied corrosion product formation on magnesium alloy AM50 with carbon microelectrodes.⁷⁶ It was found that the carbon microelectrodes had advantages, such as the ability to monitor the mediator regeneration with a hydrogen current contribution. Additional conclusions were that porosity and thickness of the insulating layer were determinable by the SECM approach curve.

The technique is also useful for studying solubilized inhibitors without organic coatings present. Singh et al., used SECM to study imidazole corrosion inhibitors for steel exposed to 3.5% NaCl saturated with CO₂.⁷⁷ SECM results agreed with the corrosion inhibition observed by EIS, potentiodynamic polarization, gravimetric, XPS, SEM, and AFM results. Tefashe et al. studied an electrodeposited coating over magnesium alloy AZ31B.⁷⁸ Tip currents from hydrogen evolution were recorded and coated and uncoated AZ31B as shown in Figure 13.

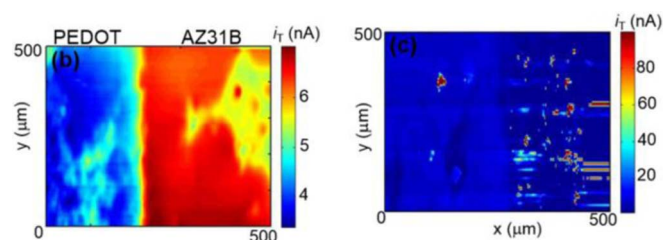


Figure 13. SECM of partially coated AZ31B after 30 minutes (left) and 24 hours (right).⁷⁸ Reprinted from the *Journal of the Electrochemical Society*.

Scanning Kelvin Probe (SKP)

Technique details.—Scanning Kelvin Probe (SKP) is a non-destructive and non-contact (no conducting path between probe and sample is required) technique which provides localized information about the metallic surfaces.⁷⁹ SKP measurements can be performed in vacuum, in open air, in humid air, or using a drop of electrolyte on the surface. The technique rasters a metallic probe usually made from tungsten metal (surrounded by brass sheath) over the metal surface at predefined speed and predefined height. The amplitude and frequency of vibration of the probe is also controlled. The vibration of probe gives rise to current which is nullified by external potential. This set up of conducting probe and substrate forms a parallel plate capacitor. The particular set up also enables the capacitive height measurements possible which in turn guides the Kelvin probe to follow the specific profile while collecting the data. Lord Kelvin first demonstrated that when two conductor surfaces are brought in electrical contact, the potential is generated. This potential depends on the work function difference in the two conductor materials. The amount of energy required to pull an electron from the conductor surface forms the definition of work function. Depending on the properties of the conductors the electrons flow to the higher work function material from the lower work function material.

In Figures 14 through 16, E_{F1} and E_{F2} are respective potentials of two plates whereas Φ_1 and Φ_2 are the work functions of respective plates. One plate can be designated as the surface of the Kelvin probe and the second plate can be designated as the surface of the sample under investigation. Figure 14 shows the two conductors which are not in contact with each other. There will not be any potential difference when two conductors are not electrically connected. Figure 15 shows

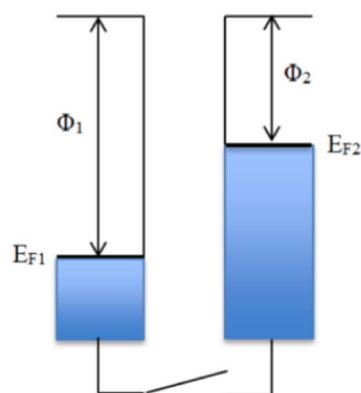


Figure 14. Charge and Energy levels when plates are not electrically connected.

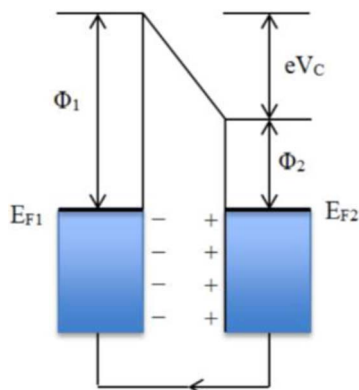


Figure 15. Charge and Energy levels when plates are electrically connected.

when the conductors are electrically connected. The resultant flow of charge results in the potential difference V_C which comes from the equalization of Fermi levels of two conductors. This V_C is related to work function by Equation 2 wherein 'e' is an electron charge.

$$-eV_C = \Phi_1 - \Phi_2 \quad [2]$$

SKP instrumentation applies equal and opposite backing potential (V_B) to nullify the potential difference V_C in two plates (Figure 16). This null condition is always sustained during the measurement to obtain the value of work function difference which is related to the potential difference in two plates. This Volta potential is directly related to the corrosion potential as shown in Equation 3.

$$\text{Corrosion Potential} = K + (\Phi_1 - \Phi_2)/e \quad [3]$$

Where 'K' is constant and $(\Phi_1 - \Phi_2)$ is the work function difference between the probe material and the substrate. The constant K for a given probe is obtained from the calibration which is performed using different materials such as copper, zinc, and iron.

One of the early versions of in house made SKP i.e. Height-Regulating SKP (HR-SKP) is shown in Figure 17.⁸⁰ which was used for obtaining the interfacial potentials for curved and rough surfaces in a controlled environment. However several modifications and improvements have been added to SKP over the years. Robust electrodes also have been fabricated for the SKP use in more demanding surroundings.⁸¹

The probe used for the SKP measurements has a diameter of approximately 150 μm which tends to provide the resolution of approximately 100 μm for the final measurement through the SKP. Sub-microscopic distinctions in potential measurements are not possible

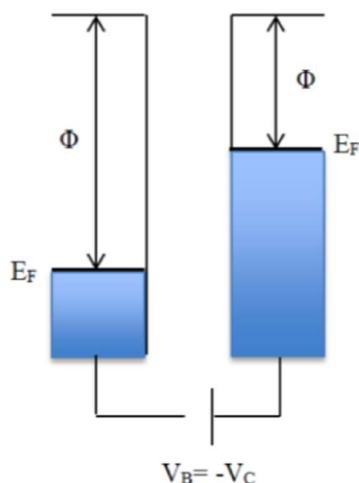


Figure 16. Charge and Energy levels when external potential applied.

with standard SKP setups.⁸² To overcome this issue, the use of an atomic force microscopy (AFM) tip for the potential measurement was pursued which is also called as Scanning Kelvin Probe Force Microscopy (SKPFM). Therefore SKPFM is the combination of AFM and SKP.⁸³ SKPFM can achieve the spatial resolution of approximately 0.1 μm with reports of resolutions even in nanometers range.⁸⁴ SKPFM concurrently measures surface topography and potential distributions. However the SKPFM measurements are more susceptible to the artifacts resulting from the tip to surface distance, surface topography, and tip surface fouling/oxidation. SKPFM probes can provide erroneous results in pitted areas and very rough areas.⁸⁵ Unusual correlations of corrosion with the potential measurements have also been found.⁸⁶ Proper experimental settings (both software and hardware), correct calibrations, and understanding of the system can help to avoid misrepresentation of the data. Such improvements have been discussed by Efav et al.⁸⁷

With the help from capacitive height measurements, pitted (with some limitations) and roughened surfaces can be measured.⁸⁸ Proper validation of the measurements and data are necessary before drawing conclusions from SKPFM measurements.⁸⁹ As surface roughness increases, work function was found to be decreasing.⁹⁰ Even though the capacitive height measurements ensure the proper measurements of work function in case of rougher surfaces, in certain cases where quantitative measurements on ultrafine boundaries are needed, techniques such as ultramicrotomy are used to ensure the smoothness of the surfaces under investigation.⁹¹

Examples of Use in Corrosion Research

Pretreatment or treatment of metal alloys surfaces before the application of the protective coatings is one of the important steps to improve corrosion resistance of hot dip galvanized (HDG) steel or other metallic surfaces. These treatments protect the substrate by either inhibiting cathodic reaction or anodic reaction or both at the same time. SKP was employed to assess the protective nature and to gain the mechanistic understanding of chromium treatment on HDG.⁹² With the help of SKP, it was found that the chromates work by inhibiting the cathodic reaction by creating the barrier for the transport of oxygen to the zinc layer. This was evidenced in the SKP measurements with the shift in the potential in negative direction for the chromium treated surface as compared to the surface which was not treated with chromium. Similar observations were made on the pure zinc surface after the application of chromate conversion coatings (also called chromate pretreatments) by SKPFM measurements.⁸³ On the delamination front, Zr based conversion coating were found to decrease the potential thereby reducing overall rate of delamination on epoxy coated carbon steel surface.⁹³ With the advent of new organic pretreatments which can modify the surface character of metal substrates, the usefulness of SKP/SKPFM for the mechanistic understanding of the overall performance for corrosion and adhesion is gaining more popularity.

Mechanical deformation leads to corrosion wear which was characterized by work function measurements by SKP on the copper surface.⁹⁴ SKP was used to detect the changes at defects arising from the mechanical stresses induced by the metal processing steps. Decrease in the local potential up to 150 mV was observed due to the introduction of plastic deformation.⁹⁵ Tensile loading caused development of cathodic and anodic sites leading to the differences in Volta potential on duplex stainless steel.⁹⁶ It was found that the residual stress in steel can decrease the passivating ability of steel alloy.³⁹

Metal alloy composition often includes several elements in trace quantities which affect the overall properties of metal alloys. Exact intermetallic composition, changes in grain boundaries, surface oxides, precipitates on the grain boundaries can impact the work function measurements and hence the corrosion performance as well.^{88,97} SKP/SKPFM is used to determine such changes in alloys.⁹¹ It is also used for investigating the impact of alloying elements on the corrosion performance of alloys in various environments.⁹⁸ Large differences in the potentials can be measured while scanning the surface of alloys. Depending on where the contrast in the potential appears, the location

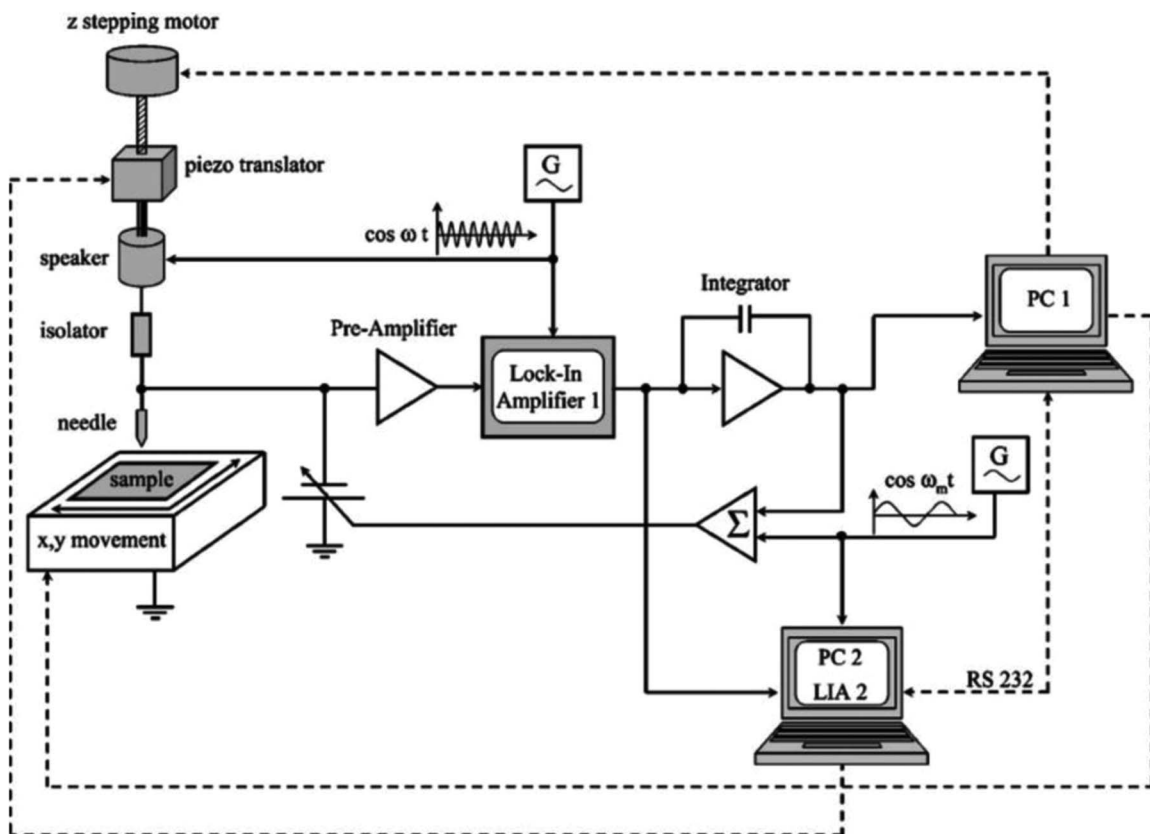


Figure 17. Experimental set-up of HR-SKP.⁸⁰ Reprinted from the *Journal of the Electrochemical Society*.

of the intermetallic particle or inclusion can be pinpointed.⁹⁹ Increases in the amount of strontium (Sr) in magnesium alloy AZ31 on its corrosion performance was found to be detrimental by SKPFM.¹⁰⁰ This causes an increase in precipitation of Al-Mn and Al-Sr phases on the grain boundaries which have different potentials as compared to the bulk of Mg resulting in increased possibility of galvanic corrosion attack. In S-65 beryllium alloy, phases consisting of AlFeBe_4 and Al_2O_3 particles exhibited the highest difference in the Volta potential with the matrix which is the indication of possibility of localized corrosion.⁸⁴ The impact of heat-treatment on steel was observed on the changes in phase boundaries and the precipitation of the more noble element on the grain boundaries.¹⁰¹ Changes in the potential were more prominent for the gradually cooled samples as compared to quickly annealed sample. Cold rolled processing of duplex stainless steel resulted in an increase in Volta potential differences in entire surface but decreased

it within ferrite and austenite phases.¹⁰² Volta potential differences in brazed and non-brazed aluminum samples were observed in sea water acidified test by SKPFM.¹⁰³ In case of re-solidified clad material, the brazing process was found to increase the Volta potential thereby decreasing the overall cathodic protection. Different corrosion mechanisms such as filiform and pitting (but not limited to) can be studied and understood by SKP/SKPFM measurements on various alloys.¹⁰⁴

Different elements in additively manufactured AlSiMg alloy showed different Volta potentials between the phases indicating the greater chance of galvanic corrosion.¹⁰⁵ Cellular darker zones in Figure 18 represents the Al in the matrix whereas lighter zone represents the Si. Phase II in the figure indicated the melt pool and discontinuous line indicates melt pool border. The Al in phase II seems to have lower potentials than phase I and Si in phase II have higher potentials therefore the difference in potentials is larger in case of phase

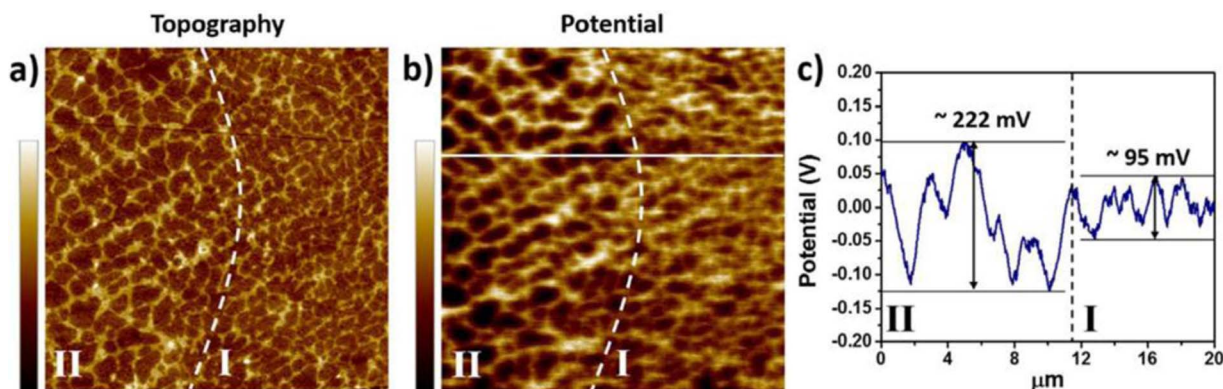


Figure 18. a) Topography and b) Potential (CPD) map (discontinuous line indicates a melt pool border). Scan size: $20\ \mu\text{m} \times 20\ \mu\text{m}$. Color bar: a) 30 nm range, b) 210 mV range. c) Potential profile of the line represented in the CPD image.¹⁰⁵ Reprinted from the *Journal of the Electrochemical Society*.

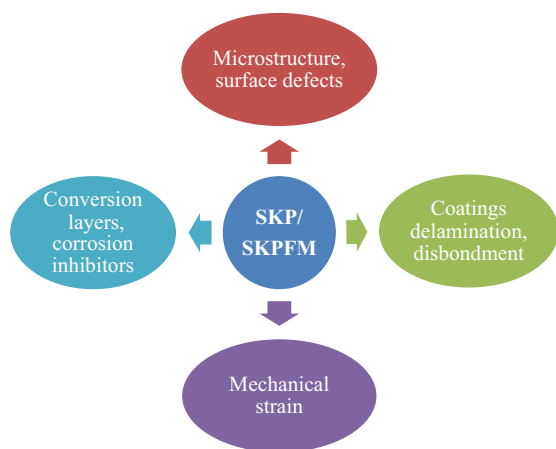


Figure 19. Applications of SKP/SKPFM in diverse areas related to corrosion.

II as shown in the Figure 18c. This difference can give rise to more galvanic corrosion in the melt pool region (phase II) in the alloy.

SKPFM has been used to study the impact of hydrogen inclusion, evolution, charging on the microstructure and the passivity of duplex stainless steel. The evidence of hydrogen presence was found at certain phase boundaries by SKP Volta potential maps which might serve as a site for the pitting corrosion initiation.¹⁰⁶ Low potential areas were detected at these places. In case of corroded aluminum 2024-T351 alloy, it was observed that the hydrogen generated by corrosion reactions found a place in the grain boundaries thereby weakening the mechanical properties of the aluminum alloy.¹⁰⁷ Hydrogen permeation, distribution, detection, diffusion, embrittlement, sorption, and desorption can be studied by using SKP/SKPFM.^{108–110}

Coating delamination and disbondment can be studied by SKP/SKPFM.^{111–113} Changes in the potential at the scribe and near the defect indicate the nature of delamination/disbondment process. Early indications of the filiform corrosion were also predicted by observing the changes in the head and the tail of the growing filiform filament. Anodes and cathodes at different local places on the surface can be identified by the SKP/SKPFM. Most of the time, diffusion of oxygen is the rate limiting factor in corrosion processes which can be very well studied by SKP/SKPFM instrumentation and methods. Smart release of corrosion inhibitors at disbondment front were studied by in situ SKP measurements.¹¹⁴ The metal and coating interface area is very dynamic and active which can be characterized by SKP/SKPFM. A SKP blister test (BT) has been developed and used to study the interface below the coated substrates and for studying the delamination as well as stability of adhesive-substrate and coating-substrate interface.^{80,115,116} High resolution (HR) SKP BT was combined with finite element simulations to establish the connection between first principles and experimental observations.¹¹⁷ Figure 19 provides the information on the applications of SKP/SKPFM in diverse areas related to corrosion.

Scanning Ion-Selective Electrode Technique (SIET)

Technique details.—The Scanning Ion-Selective Electrode Technique (SIET) provides real time measurements of pH and/or existence of particular ionic species above the surface in electrolyte in a non-invasive manner.¹¹⁸ SIET technique consists of a microelectrode which is a micropipette made from glass or plastic which contains ionophore for the detection of changes in the pH or ion detection at the tip of electrode. Some initial work on ion-selective microelectrodes is described by Ammann.¹¹⁹

The typical set up for SIET measurement is shown in Figure 22 (minus the SVET vibrating probe). The measurement also employs external reference electrode which is generally a wire Ag/AgCl reference electrode. The micropipette along with reference electrode are

mounted on the 3D stepper motor system which is controlled from the computer. The tip size is of 0.1 to 5 μm which provides good lateral resolution.^{120,121} The sample to be examined is immersed in the electrolyte and both the electrodes are brought in the vicinity of the sample. The optics of camera assisted with video helps to capture the sample image, helps in positioning the probe, and maintains the distance between sample and the probe. It is also used heavily in the calibration of the microelectrode which needs to be done before and after the measurement in the case of SIET. The micropipette moves on the sample surface. The motion, speed, and area to be covered by micropipette are controlled by computer. The data can be plotted as 3D data representing the distribution of pH or ion concentration over the sample are under investigation.

SIET measurements are performed in potentiometric control. The potential variations due to changes in ionic concentration are measured in this potentiometric control mode.¹²⁰ Ionophore membrane used in ion selective electrode are selected based on their ability to allow particular ions through the membrane. The ions, which diffuse through the membrane, cause the changes in the chemical potential and hence potential difference which in turn are detected with the help of internal reference electrode and external reference electrode.

Use of ion selective electrodes have their own limitations. The glass micropipettes are brittle and hence fragile. Transparent nature of glass makes it difficult to achieve proper distance between probe and sample during the measurement as well as in the calibration process. Micropipettes can foul and corrosion products can block the tips which limits how long the electrodes can be used. Preparation of micropipettes is laborious and requires a skillful hand. Solid contact microelectrodes have been developed which can address some of these issues.¹²⁰ Keeping electrodes as close as possible to substrate can minimize large ohmic drop in the solution.¹²¹

Examples of Use in Corrosion Research

SIET was used in the measurement of pH over the surface of an epoxy which was embedded with the galvanic couple of aluminum and copper and exposed to 0.01M NaCl solution.¹²² Acidic pH was observed due to the oxidation of aluminum (anodic dissolution leading to hydrogen ions generation) and alkaline pH was observed on the surface of copper due to the reduction reaction happening on the copper surface (due to generation of hydroxyl ions). This use of SIET in detecting exact change in pH on the surface of different metals is helpful for detecting the interactions between those metals. This application can be extended to various combinations of galvanic couples in different electrolytes. For the detection of changes in pH, the hydrogen ion (H^+) selective electrodes are used. The pH response can routinely vary between 5 and 12 depending on the acidic and alkaline regions.

On the coupled surface of Al and MgZn_2 , pH response was measured by SIET at pH 4 and then at pH 6 in 0.1M NaCl solution after 1.5 hours of immersion as shown in Figure 20 at a pH 6, greater separation in the anodic and cathodic activity was obtained. In the high pH range, Mg corrosion products form. Self-dissolution of Mg in high pH region is supported by the pH ranges observed on the entire surface.¹²³

Ion selective electrodes can be fabricated for the detection of specific ions coming off the surface of the metal or substrate. Magnesium ions were detected by specially fabricated Mg^{2+} ion sensitive electrode.¹²⁴ Depending on which ion to be detected, the appropriate ionophore is selected. Several ions such as H^+ , Cl^- , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Ag^+ , NH_4^+ , and Cu^{2+} can be detected with the help of specially fabricated ion selective electrodes.¹¹⁸ Changes in the pH due to corrosion reactions can signal the activation of particular corrosion inhibitor for the purpose of corrosion inhibition. Knowing which counter ion is being released in the event of corrosion reactions can help to deduce the nature of corrosion mechanism. Use of corrosion inhibitor 1,2,4-triazole over the surface of magnesium maintained the pH in defect in neutral range providing the much needed corrosion protection.¹²⁵ It was possible because the corrosion inhibitor decreased the activity of hydroxyl ions in the defect area.

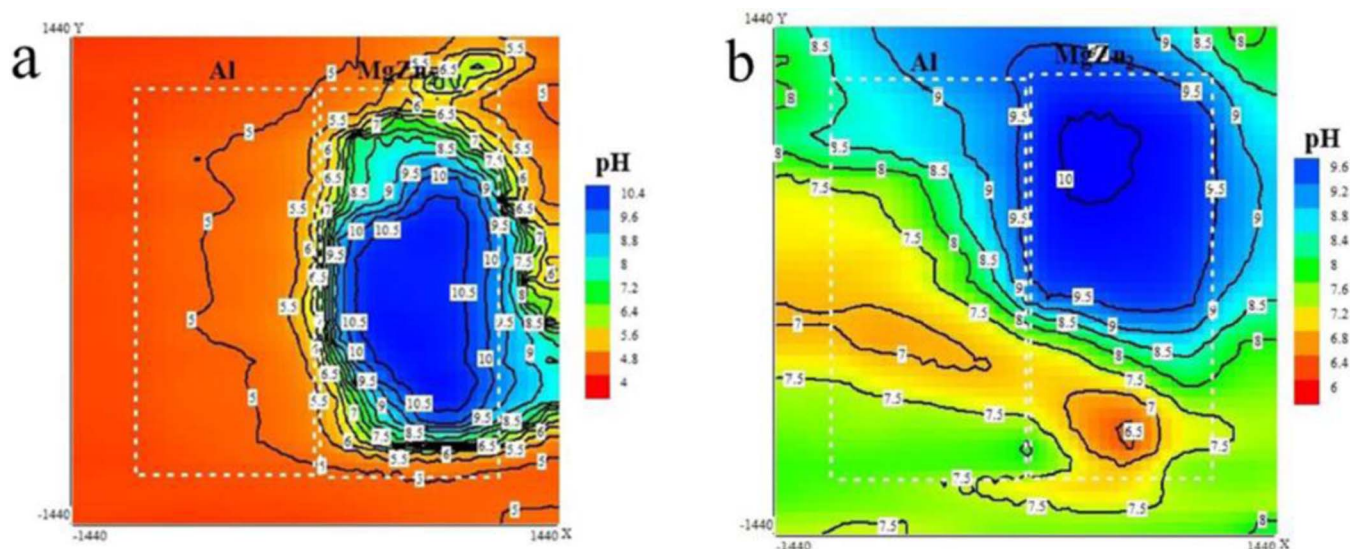


Figure 20. SIET pH distribution maps of Al/MgZn₂ couple at (a) pH 4 (b) pH 6 after 1.5 hours in 0.1 NaCl solutions.¹²³ Reprinted from the *Journal of the Electrochemical Society*.

Zinc is important element which is used in the corrosion protection of steel surfaces. Substrates such as hot dip galvanized steel, Galvalume and coatings such as organic and inorganic zinc rich primers form a sizable portion of strategies for the protection of steel from the corrosion. Zn²⁺ ion selective electrode was developed and used for the characterization of different stages of zinc dissolution in the solution.¹²⁶ It is possible to map two ions simultaneously by using two different ion selective probes in the same solution. The presence of counter ions in the same medium affects the corrosion mechanisms therefore mapping counter ions such as Na⁺ and Cl⁻ at the same time is of much importance. A dual head stage micromanipulator was used to have two ion selective electrodes in the solution. Depletion of Na⁺ and increase of Cl⁻ was observed at the anodic sites. Due to the presence of H⁺ ions, the counter ion Cl⁻ could be migrating to the site of increased H⁺ ion concentration. This Cl⁻ sustains the continuous anodic dissolution.^{120,127} This information on localized level helps to understand the impact of ion migration, deposition, and participation in the corrosion process. Combination of 3D pH maps along with the optical image and ion distribution map is a powerful tool to understand the corrosion processes happening on the surface. This information can be combined with the current density maps obtained by SVET technique to provide more useful data. SVET-SIET combination studies are summarized in the section on use of combined techniques later in this paper.

Scanning Droplet Cell (SDC) Technique

Technique details.—The necessity to use Scanning Droplet Cell (SDC) stems from the fact that the area of electrolyte influence can be limited to the single droplet on the surface. Surface tension forces then hold this droplet on the surface which can be dragged across the sample by means of capillary. This set up allows researchers to perform wide range of electrochemical experiments in three electrode cell configuration on a very small area (droplet contact area to surface) compared to the high area of measurements used in traditional global electrochemical techniques. The contact area of droplet to the surface could be as low as few microns.¹²⁸ Size of capillary could be as small as nanometers.¹²⁹ The microcapillary holder which is typically manufactured from plastic holds in place the three electrode set up. Recently some capillary holders are being made with 3D printing technology.^{128,130} One of the improved and high throughput version of SDC called Scanning flow cell is shown in Figure 21.¹³¹

As the area of the sample measurements is very small, the currents generated are very small (current in the range of picoampere). This level of sensitivity in the measurement can be achieved by a modern high resolution potentiostat. The microcapillary tip is prone to blockage/leakage as well as breakage. High quality SDC holders along with experimental parameters modifications can help to avoid damage. The ohmic drop should be taken into count as well even though moving the droplet on the surface is quite dynamic process. Keeping all electrodes as close as possible and the miniaturization of set up helps to alleviate this issue.¹²⁹

Examples of Use in Corrosion Research

SDC techniques have been employed for the characterization of corrosion behavior of metal surfaces including the oxide layers which are present on metals such as aluminum. Micro-electrochemical measurements by using SDC and macro electrochemical measurements were performed and compared on 304L stainless steel surface.¹³² Tafel measurements performed at micro scale by SDC technique exhibited

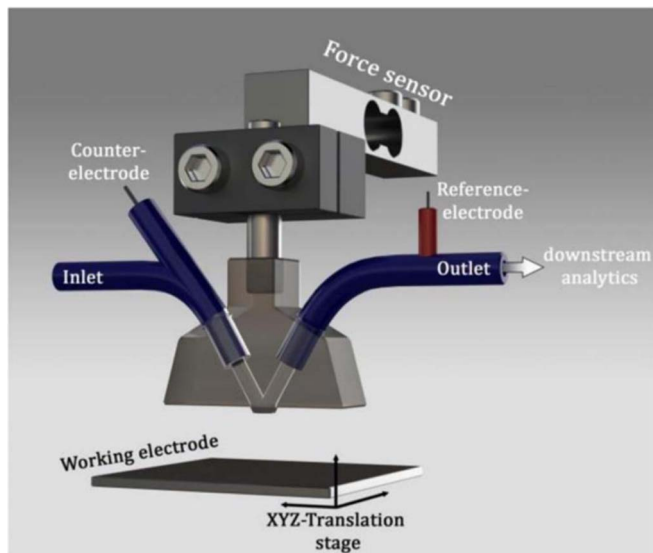


Figure 21. Diagram of Scanning flow cell (SFC): A high throughput version of SDC.¹³¹ Reprinted from the *Journal of the Electrochemical Society*.

lower potentials than that at macro scale. This change was attributed to the decrease in exposed surface area at microscale. Electrochemical impedance measurements performed on micro and macro scale were fitted with different circuit modes indicating divergent diffusion phenomenon happening at the two levels. When the potential measurements were performed on the copper covered steel surface, at the defect, -600 mV of potential was observed whereas everywhere else value of potential around -300 mV was observed. These defect areas can then initiate corrosion.

Polycrystalline FeAlCr alloy was investigated for the impact of orientation and grain boundaries on the current density behavior by SDC technique.¹³³ Anisotropy, which results from different crystal orientations, were found to exhibit varying critical current densities indicating their changing corrosion response. $\{001\}$ was found to have higher critical current densities than that of $\{111\}$. Oxide layers and grain packing were also found to influence the corrosion tendencies by using microelectrode technique based electrochemical measurements.¹³⁴ It was found that the grains of certain orientation undergo oxidation at different rates. Impurities which generally tend to deposit/migrate at grain boundaries also affect the surrounding grains. Pit nucleation was strongly influenced by the changes at the crystal levels and these were easily characterized by SDC technique. Inclusion of certain elements either enhance or have an impact on the pitting process. This was observed in case of molybdenum free stainless steel where in the presence of MnS inclusions did not affect the pit nucleation activity.¹³⁵ It was found that the pits were initiated at the interface of inclusions such as (Ti, Ca)-oxide.¹³⁶ Different phases, such as ferrite and austenite, also exhibited distinct electrochemical behavior at the boundaries. Depletion of certain elements, such as chromium and molybdenum, as a result of precipitation was found to decrease the corrosion resistance in super duplex stainless steel because of heat-treatment.¹³⁷ All of these changes in the deposition/depletion of certain elements as a result of some treatment to the metal or alloy can be easily detected by using SDC set up.¹³⁸

SDC technique was modified to have a constant flow of electrolyte as it drags over the substrate.¹³⁹ It was termed as f-SDC wherein “f” stands for “flowing”. This modification was introduced to avoid the contamination of electrolyte due to the contact with substrate and to provide fresh supply of electrolyte during the entire measurement. f-SDC was used to obtain corrosion potential measurements on automotive grade aluminum alloy brazing sheets. Changes due to sacrificial metals (due to presence of zinc) in this alloy was observed in the corrosion potential measurements which ultimately affect the corrosion tendencies of this alloy.

Combined use of techniques.—One or more localized electrochemical techniques are often combined together to obtain more electrochemical information about the system in complementary manner. Simultaneous use of techniques not only validates the results obtained by single techniques but also provides multifaceted solution to the problem being investigated. SVET and SIET are combined to obtain current density, pH, and concentration of certain ions in the same system concurrently. SKP and AFM are combined to form a new measurement technique called SKPFM which is used to obtain Volta potential with the resolution of AFM instrumentation. LEIS is a special case where a global electrochemical technique such as EIS is combined with local microprobe technique to obtain the impedance at local level. Simultaneous LEIS and SKP measurements are also performed. SDC adaptation allows the DC measurements as well as AC measurements one after another with same set up. As most of the localized techniques are probe techniques, they can be combined in the single instrument however there is a compromise of how many techniques can be used concurrently and how to optimize such a system for the various techniques.

Figure 22 shows the combination of SVET and SIET techniques. Wherein, the SVET probe is an insulating Pt-Ir vibrating probe with Pt ball at the tip along with ionophore containing SIET micropipette probe. The calibration probe is also shown in the Figure 22 along with the pseudo reference electrode. The sample is generally 1 cm x 1 cm

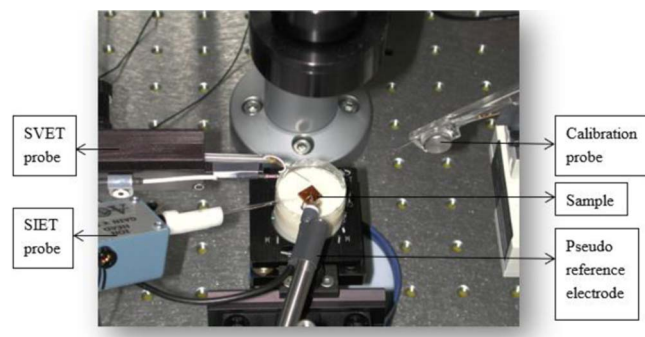


Figure 22. Combination of SVET and SIET techniques.

in the dimensions kept in the electrolyte of interest. The SVET-SIET combination was used for investigating the effectiveness of corrosion inhibitors (either in coating or in solution) for the corrosion protection on various metals. Corrosion response on the galvanized steel surface dip coated with silane films comprising of $\text{CeO}_2\text{-ZrO}_2$ was evaluated by simultaneous SVET-SIET technique.¹⁴⁰ Lower current densities were observed in the scratched area of the nanoparticles containing films compared to blank films after exposure to 0.005M NaCl solution. Mild acidic pH was found in the scratched region and increased pH in the cathodic regions elsewhere over the coated surface were noted which was complementary with the SVET results on the same areas. Several sol-gel films containing inhibitors such as 1,2,4-triazole, F^- and Ce^{3+} were measured for corrosion protection on magnesium alloy AZ31 in 0.05M NaCl.¹²⁵ It was found that in defect areas, 1,2,4-triazole containing sol-gel coating maintained lowest current with immersion and also maintained the pH in the neutral region thereby inhibiting the corrosion. CeO_2 nanoparticles containing silane coatings were found to provide corrosion protection to the magnesium alloy AZ31 by self-healing mechanism.¹⁴¹ Decreased current density in the defect and limiting the increase in pH in defect region ensured improved corrosion protection. Corrosion products of magnesium were stabilized due to participation of CeO_2 nanoparticles in the formation of protective layer.

Containers with several different corrosion inhibitors were incorporated in a weldable primer and it was applied on galvanized steel.²⁷ In the defect area, samples containing the corrosion inhibitors showed lower current densities and near neutral pH in cathodic areas. Whereas blank sample showed very high current densities and acidic pH in anodic areas and basic pH in cathodic areas. The decrease in pH in anodic areas indicates the dissolution of zinc as well as iron. Decrease in current density was attributed to the passivation of zinc and self-healing ability of corrosion inhibitors. Plasma electrolytic oxidation (PEO) generated oxide film containing 8-hydroxyquinoline on the surface of magnesium was found to decrease the current density by 30 fold.¹⁴² It was also found that the corrosion inhibitor was activated once the pH was became basic in the cathode areas providing additional corrosion protection.

Different phases in metal alloys and their impact on the corrosion processes can be studied by simultaneous SVET-SIET measurements. S-phase in aluminum alloy AA2024-T3 was simulated by using Al-Cu-Mg as a model system.¹⁴³ It was found that the cathodic processes occurred mostly on Cu and Mg whereas the anodic processes were observed on Al and Al-Cu interface (as evidenced by the dissolution of Al). In the similar studies it was also found that Al dissolves because of decrease in pH.¹⁴⁴ Much of the Al phase is lost because of alkalization of S-phase. Cut edge corrosion of galvanized steel is where both zinc and iron are exposed, zinc acts as anode and iron acts as cathode.¹⁴⁵ At certain critical pH (8–11), as Zn^{2+} becomes insoluble and the corrosion products precipitate which was evidenced by the decrease in the current density. In this way mechanism of the corrosion action in several alloys can be studied. Simultaneous measurements of current density, pH, and dissolved oxygen were carried out in

another study in Al-Zn-Mg on the steel surface.¹⁴⁶ In another study, Al was coupled with MgZn₂ intermetallic particles to study the galvanic interactions.¹²³ At different pH, the respective element in the couple exhibit different dissolution behaviors.

Combined ionic current, pH (by potentiometric microelectrode), and O₂ reduction measurements (amperometry) were obtained concurrently for testing the addition of corrosion efficiency of Ce³⁺ in the sol-gel coating on AA2024-T3 substrate.¹³ The impact of addition of Ce³⁺ on the corrosion protection in the defect was studied. Standard anode/cathode combination was observed via SVET before the addition of inhibitor whereas decrease in current was observed after the addition of corrosion inhibitor indicating the corrosion protection. Also, a slightly basic pH signified the formation of hydroxyl ions before the addition of inhibitor in the defect. Reduction of O₂ in the defect site also showed the consumption of O₂ in the defect for cathodic reaction.

Scanning Ion Conductance Microscopy (SICM) measures the ion flux by tracking the conductivity changes.¹⁴⁷ It provides surface electrochemical activity information along with topography details. SICM can be used standalone or can be combined with SECM.¹⁴⁸ SECM has been simultaneously used with AFM for the electrochemical imaging of the copper surface.⁵⁹ SECM was combined with high resolution SKP to study the impact of intermetallic particles on the galvanic interactions and localized corrosion processes.¹⁴⁹ Apart from the simultaneous/concurrent use of the techniques, multiple localized electrochemical techniques are often used separately in the same study for electrochemical corrosion characterization purpose.

Concluding Remarks

This paper presents a concise description of localized electrochemical techniques along with their applications. For each of the technique such as SVET, LEIS, SECM, SKP, SIET, and SDS, the advantages, disadvantages, brief theory, instrumentation, and practical set up has been provided. The promise of these techniques rests on the fact that, these techniques provide mechanistic information on local scale which cannot be obtained by global electrochemical technique. Even though useful information is obtained by these techniques, the training requirements, understanding of nuances of the measurements, time taken for the calibration and set up of sample could pose a challenge to a researcher.

Combined use of techniques is on the rise however often times combining more than two techniques simultaneously is difficult. Within a single instrument, several techniques can be combined. In that case often times the measurements need to be done one after another instead of simultaneously. The great advances in the techniques over the recent years will surely continue with further improvements to both the instrumentation and software. Even though there is considerable corrosion research published based on these techniques, they are still not mainstream techniques. Refinement of the techniques so that standardized protocols (ASTM, ISO etc.) can be developed would push their use beyond the academic laboratory.

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