Application Note SECM370-2

Subject: Scanning Probe Application Constant Current Macro

Scanning Electrochemical Microscopy Macro for Constant Current Mode

Introduction

The SECM constant-current macro allows a user to successfully approach a surface, specify a current set-point and track that set-point across the surface. This macro-template combination installs with version 1.03 and later of the Macros file in combination with the M370 software and the SECM370 module. Setup, operation and common issues are discussed within this document.

The constant current macro is designed to work on homogenously conducting or insulating surfaces using the approach-curve feedback data obtained at the start of the experiment. Effectively, this makes the constant-current macro a combination of two separate experiments; an auto-approach curve experiment and a current-tracking area-scan experiment. The auto-approach curve experiment provides a known current/probe-distance relationship that the current-tracking experiment uses to determine its location. This remains true provided the surface characteristics do not change. Thus, if the conductivity of the surface does changes across the sample, the current versus z-location will no longer hold true for that part of the sample and the position changes will be erroneously calculated. However, providing the sample homogeneity condition is met, a user will be able to take a topographical map of their sample.

Apart from taking topographic images of surfaces, the most obvious use for this technique is to map a sample surface before some 'surface activation' takes place and before an SECM images is taken, and again after some 'surface passivation' takes place. This can be used to help distinguish between topographical changes and electrochemical or conductivity changes.

Figure 1 below shows the experiment and configuration screens for these experiments. The 'X-steps' and 'Y-steps' and 'X step-size' and 'Y step-size' define the total area over which the experiment will take place. Ensure you select a probe potential at which an oxidation or reduction reaction occurs in the system under study; it is possible to erroneously select a potential where no current will flow, resulting in no ability to detect a surface. To avoid this, perform a CV experiment and from this choose a potential that shows a reaction. See Figure 1 for an example.

Configuration and Setup

Figure 1 below shows the configuration box for the Area-OCP experiment.

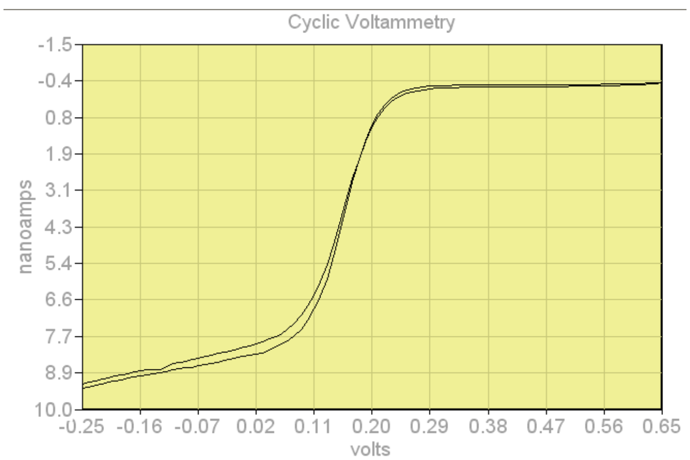

FIGURE 1: A CV on a 15-µm probe. Selecting a potential that reduces the product is a sensible choice in this case (for example at -0.25 volts). Positive voltages between +0.2 and +0.65v produce no current flow in this system, so should not be used.

It should be evident at this point that the potential chosen produces a current flow and a corresponding diffusion field around the probe tip that can be enhanced or inhibited by the sample, and that this diffusion field is the mechanism through which the probe tracks the surface. It is also possible to set a potential on the sample – if the edit-box ‘Use Sample’ is set to ‘0’, the sample will not be set to the selected potential, set this to’1’ to otherwise polarize the sample as defined in ‘Sample Potential’.

The ‘probe size’ is an important factor for this experiment; this dictates the overall step size for approach curves and the maximum step taken in the current-tracking area scan phase of the experiment. If this is entered incorrectly, it is possible that the step size chosen to attain the desired current will be overestimated and result in too-great a movement in the probe tip either towards or away from the surface. The value required here is the diameter of the metal at the probe tip. Here, a platinum probe of size 25 microns has been specified.

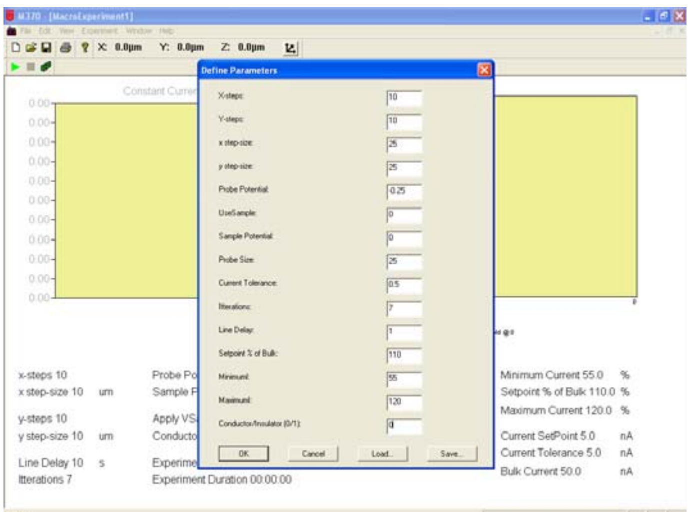

FIGURE 2: Experiment configuration screen

The ‘current tolerance’ value (in nanoAmps) is used in conjunction with the ‘Iterations’ parameter according to the following criteria –

1. If the current measured is outside of the ‘current tolerance’ of the current sought, the instrument will repeatedly search the z-axis, according to the original approach curve, for the desired current up to ‘Iteration’ number of times.
2. If the current sought cannot be found within the tolerance specified after ‘Iteration’ number of z-axis movements, the final current value will be recorded.

The values defined in ‘Minimum I’ and ‘Maximum I’ are used solely in the auto-approach curve phase of the experiment. The values are “% of bulk current”, so for an approach to an insulating surface the instrument will halt when the current reaches 55% of the bulk current, as shown in Figure 2 above. An experiment set to approach a conducting surface will halt when 20% above the bulk current is achieved (indicated by ‘120%’ in Figure 2). Here, 100% is the current seen by the probe in bulk solution, or bulk current for short.

An important point not to miss here is that the probe must start in the bulk of the solution to acquire a ‘bulk current’. As the enhancing/inhibiting effect of a surface can be first seen to affect the probe current at three to four times the platinum diameter from the surface, it is recommended that the probe start at least five times the platinum diameter from the surface. For example, a probe with a 25µm platinum core should be at least 125µm from the surface.

The parameter ‘Conductor/Insulator (0/1)’ will set the system to use the ‘Minimum I’ or ‘Maximum I’ value to terminate the approach curve part of the experiment normally. Here, ‘0’ represents a conductive sample which should give the expected current enhancement at close probe-surface proximity.

Similarly, a ‘1’ represents an insulator which should give the expected current inhibition at close probe-surface proximity. With either sample type, the ‘Minimum I’ and ‘Maximum I’ will stop the experiment, however, the experiment will only continue normally into topographic-scan mode if the expected inhibited or enhanced trend is seen.

The ‘Setpoint % Of Bulk’ is the value used by the macro to calculate the current that should be tracked across the surface. This is of course proportional to the distance between the probe tip and the sample, as defined by the approach curve. This value must be set between the ‘Minimum I’ and ‘Maximum I’ limits, and must be greater than 100 for a conductor and less than 100 for an insulator. The macro will check that these constraints are met before it will allow an experiment to run.

Finally, after a complete line of a topographic scan has been completed, the probe will return to the start of the next line before starting the next scan. As the probe tip returns to the start of the next line at a much faster rate than the speed moved between points, the solution is stirred more than normal and the resulting current measured (without a delay) will be considerably larger than a normal step. The consequence of this is that the current reading makes the probe appear further (insulator) / closer (conductor) to the surface than it actually is. Adding a ‘Line Delay’ to allow the solution to settle

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before the new measurement is made increases the reliability of the measurement and reduces the amount of 'hunting' for the set-point. For the 25micron probe example shown in Figure 2, a 1 second delay is sufficient in most cases. Larger probes may require longer delays to settle.

Whether a sample's topology is known or not, it is a good starting point to perform the normal SECM set-up procedure:

- Mount the sample on a sturdy base.
- Insert and secure the sample/base into the tricell or micro-tricell.
- Ensure the electrodes are clean before use.
- Level the sample using a spirit-level if possible.
- Alternatively, try to level the sample using electrochemical techniques.

Having a level sample is a good starting point for an unknown surface as slopes too steep may cause the tip to crash. This results from the platinum at the center of the probe tip not registering the collision of the glass at the extremities of the glass defined by the RG ratio. Of course, this will also be the case for large step-changes in topology; however, it is possible to prevent most slope problems by careful consideration of the sample, experiment and probe setup. Starting with a level sample is also useful when progressing from the Constant-Current experiment to a standard SECM area-scan experiment.

Finally, choose your step-size for the area scan based on your probe size, RG ratio, distance from the surface and an estimate of the sample maximum slope/step change. Figure 3 shows a simple view of a probe in close proximity to a surface.

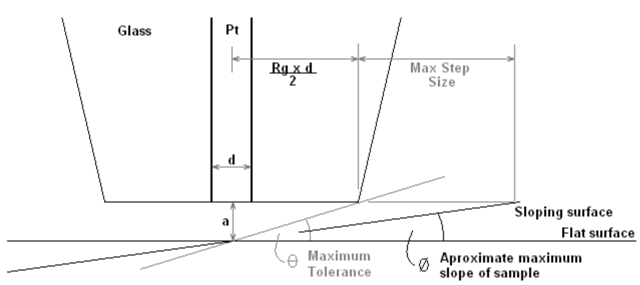

FIGURE 3: For a probe set at 'a' from the surface, the maximum tolerable slope without impact is equal to *Tan^{-1}(2a/(d RG))*. The maximum step size requires either a judgment to be made by the operator, or a set-up line-scan performed at high resolution over part of the sample to determine Φ. Max step size = (a / *Tan* Φ) – (RG x d / 2)

For example, a 25micron probe with an RG of 10, set at 15microns from the surface over a sample with approximately 3° slope should be limited to step sizes no more than 160microns. Step changes in height should be limited to less than the probe to surface distance where possible. Samples that have some 'give' in them (soft surfaces etc.) may be able to exceed this.

The above procedure will help to limit probe crash situations when the sample topology changes by large amounts over a short distance. Also, it is advisable to use as a preference, values fairly close to 100 for "Set Point % of Bulk", for example, 90% – this means the probe is only just 'feeling' the effect of the surface and is more distant from the surface resulting in a scan more forgiving to topology changes. A counter-point to this is the fact that the same current tolerance will result in larger positional tolerances if used to track the surface at a larger distance.

Figure 4 shows a setup for an insulating surface, and Figure 5 the setup for a conducting surface.

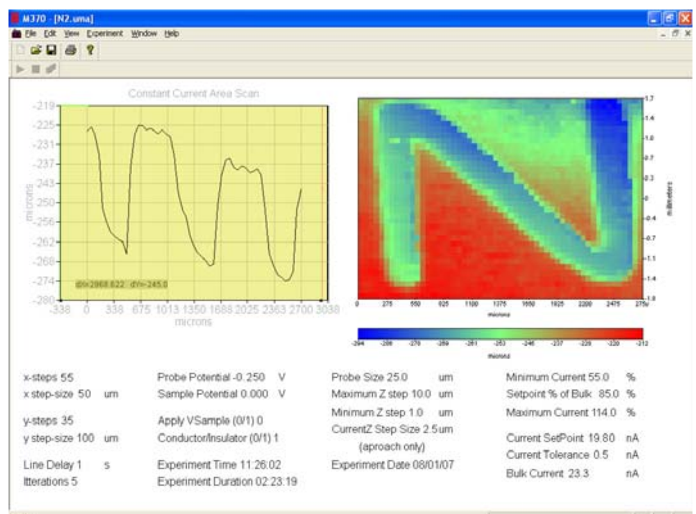

FIGURE 4: Results from an example experiment tracking the topology of an insulating surface. Here, the impression printing of a letter 'N' is shown.

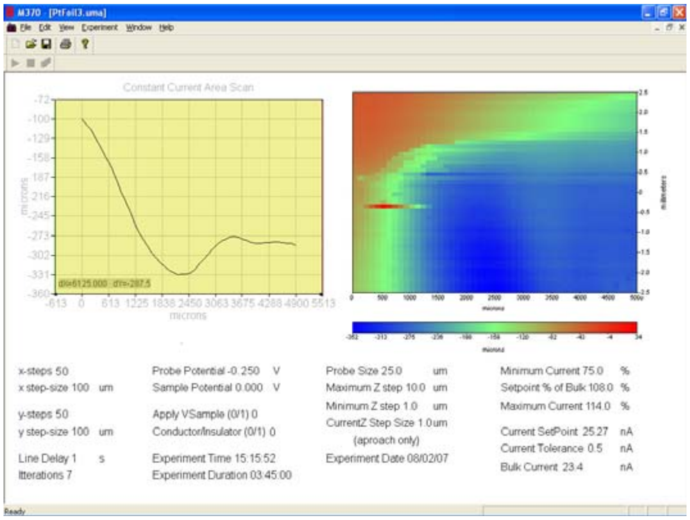

FIGURE 5: Results from an example experiment tracking the topology of a conducting surface. Here, the topology of a Pt foil is shown.

Potential Problems

The most common problem with the Constant-Current macro is that of the probe 'hunting' for position. Commonly, the probe will find its target current in around 2 – 4 iterations during the course of a successful run (when a current tolerance in the region of 0.5 to 1nA is specified). There are a number of reasons why this may not be the case:

- The conductivity of the surface has changed. This may be due to impurities in solution (dust, hairs, *etc.*) or may be due to air bubbles on the surface. It may also be possible that films are forming on the surface of the sample or probe during the course of the experiment.

- If the surface of the sample is sloping beyond that tolerable by the probe and step-size, the probe can contact with the surface causing the sample to move, the probe to move, and/or not being able to find the current set-point. This is also the case for large step-changes in topology.

- Too-large a step size can cause a stirring effect that causes the first few readings to see incorrect current values, until the solution settles. How susceptible a probe is to this is heavily dependent on its size and the step size made. Larger probes are more susceptible to this effect.

The procedures outlined can help in identifying the cause of problems caused by variation in samples and experimental parameters.

Figure 6 shows the results from Figure 4 plotted in a 3D environment using the Isoplot software package.

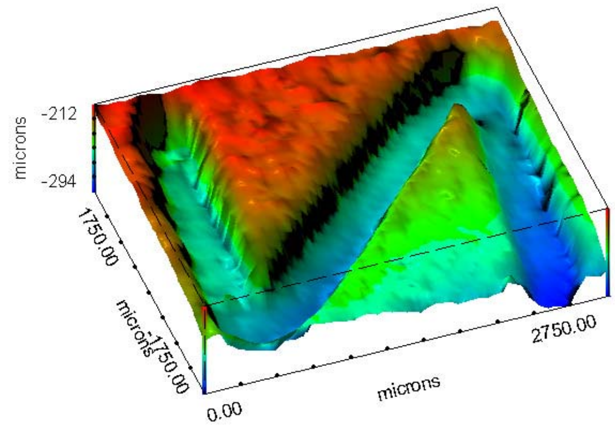

FIGURE 6: Inverted data in a 3D environment using Isoplot.