Application Note SECM370-1

Princeton Applied Research

Subject: Scanning Probe Application Area OCP Macro

Scanning Electrochemical Microscopy Macro to Measure OCP

Introduction

The SECM Area-OCP macro allows a user to measure the small variations in the open-circuit potential as a function of position within a defined area. This is a macro-template combination which requires adding to the M370 root directory (i.e. c:\M370\). Setup, operation and common issues are discussed within this document.

This macro is intended to be used in a similar way to all other area-scan type experiments. However, in contrast to the other area mapping techniques which measure current, this is the first area-mapping macro that measures the potential. The fundamental requirement for a successful application of this technique is the active site, or surface. In the case demonstrated here a common point-in-space (PIS) sample, composed of a 200µm platinum wire embedded in epoxy, is used to provide an active area which has a -250mV potentiostatically controlled voltage applied to it, resulting in a continuous current of ~+160nA. This current will in turn cause an electric field throughout the solution that can be measured with a standard SECM probe. This setup is useful in mimicking common conditions such as those seen in corrosion where localized anodes and cathodes produce the active sites. It is of course possible to emulate this setup here by applying a potential to the sample to accelerating a sample's corrosion rate. This would normally be done with the secondary potentiostat, either manually through the front interface of the potentiostat or by accessing the menu options 'Experiment' and 'Set Secondary Potentiostat'.

Configuration and Setup

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

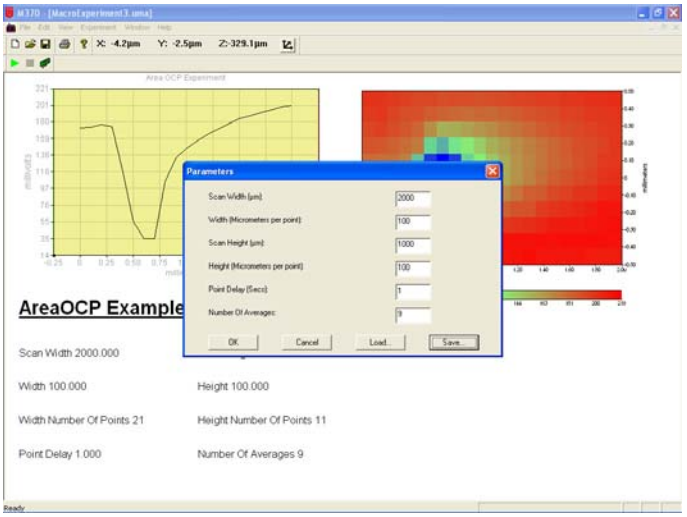

FIGURE 1. The Area-OCP configuration screen.

The set-up for this experiment is similar to other area-scanning experiments:

- 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.
- Approach the surface using the standard techniques.

The configuration parameters for this experiment are self-explanatory; Scan Width and Scan Height, along with the Width (Micrometers per point) and Height (Micrometers per point) define the area to be scanned. The Point Delay (Secs) refers to the time between a step taking place and before the acquisition starts. Finally, the 'Number Of

Averages' allows the user to discriminate against background noise by enhancing the signal to noise ratio. The setup shown in Figure 1 shows a lopsided line-scan trace of the PIS sample. This is due to two effects; stirring of the solution as the probe scans through the diffusion field, and the geometry of the electrode setup. Increasing the point-delay should reduce the effects of stirring, and this in turn depends on the size of the electrode; larger electrodes generate larger diffusion fields that are less resistant to the effects of stirring and require longer times to settle. Also, in the configuration above the counter-electrode (CE) is placed at the right hand side of the electrochemical cell resulting in a skewed electric field. This results in a predominant flow of ions/mediator between the active PIS sample and the CE source. The use of a circular CE that surrounds the sample should then produce a more-evenly distributed OCP measurement.

Figure 2 shows the result plotted (inverted) in a 3D environment using the Isoplot software package.

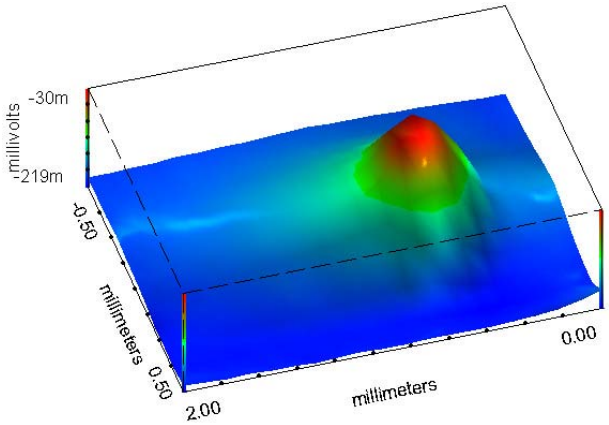

FIGURE 2: Inverted data in a 3D environment using Isoplot.

Additional Applications of this Macro

This document details the "Area OCP" macro that installs with the latest version of the M370 software. If you have the SECM370 module, an upgrade to a version with this and other advanced macros for experiment sequencing, etc. is available for free download. Installed macros are accessed on the tab labeled "Electrochemistry" in the M370 software.

Here a standard Pt probe was used to measure this OCP value. However, if this standard probe was replaced by an ion-selective electrode, this would allow you to measure local ion-specific concentrations, such as local pH across the measurement plane or local ion-diffusion fields such as those of biological interest (e.g., Ca^{2+} or K^{+}).