# PicoLE Electrochemistry Tools User's Manual

v1.0



Molecular Imaging

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## Electrochemistry Overview

The electric potential that exists across the interface between a metal surface and an electrolytic solution (also called the surface potential) is the driving force behind such processes as adsorption, desorption and electron-transfer reactions. Quantifying and controlling this potential is the science of electrochemistry. Metal electrodes placed into the electrolytic solution will only register a net potential that is composed of two unknown potential drops, one across each electrode-electrolyte interface. For this reason a third, reference electrode must be used. The reference electrode is a chemically reactive electrode maintained in equilibrium with the ions (in solution) that are oxidized and reduced at its surface. To maintain this equilibrium, the concentrations of the reactants must remain constant at the electrode surface, a condition established by ensuring that negligible current flows through the reference electrode.

# Equipment and Setup

The equipment needed to perform electrochemistry experiments can be as simple as a liquid cell and a few electrodes, or as complex as a flow-through pump system with a temperature-controlled sample stage. This module covers the liquid cell and electrodes. If assistance is required in setting up or designing an experiment, contact Molecular Imaging at support@molec.com. Application scientists will gladly be of assistance.

The PicoStat Controller must be connected (via the DB25 cables) between the PicoScan Controller (tower) and the PicoLE Head Electronics Box. See the appropriate **Connection Diagram** for the system, and options being used with that system, in the **Schematics module**.

## Cleaning and Preparing Cells and Electrodes

The liquid cell supplied for the PicoLE microscope is 15 mm in diameter. The sample surface must be very flat and larger than the diameter of the cell to avoid liquid leakage.

The liquid cell should be cleaned prior to use. There are many methods for cleaning. Two are listed below.

### Non-Critical Applications

1. Sonicate the liquid cell in laboratory detergent.
2. Rinse in 18 MΩ·cm water – rinse toward the tweezers.
3. Rinse in methanol.
4. Blow dry under Ar or $N_2$ gas.

### Critical Applications

1. It is important that all glassware be thoroughly cleaned, or it will be of no value to clean apparatus; therefore, it is important to first follow these procedures for all **glassware** that is to be used.
2. Soak overnight in a solution of 70% concentrated sulfuric acid and 30% hydrogen peroxide (of 30% v/v concentration). USE EXTREME CAUTION HANDLING THIS SOLUTION, IT IS EXTREMELY CORROSIVE AND A STRONG OXIDIZING AGENT.
3. Rinse thoroughly at least four times in 18 MΩ·cm water.
4. Boil for one hour in 18 MΩ·cm water, changing the water every 15 minutes.
5. Instead of step four you can rinse overnight in 18 MΩ·cm water.
6. Rinse two more times in 18 MΩ·cm water.
7. Dry under Ar or $N_2$ gas.

## Electrodes

Prepared electrodes may be purchased from Molecular Imaging, or wires may be formed into appropriate electrodes using the following approximate dimensions. The type of wire of which the reference and counter electrodes are made will affect the voltage readings.

**Reference Electrode (RE)**

The reference electrode should be silver with a diameter of 0.51 mm (0.02").

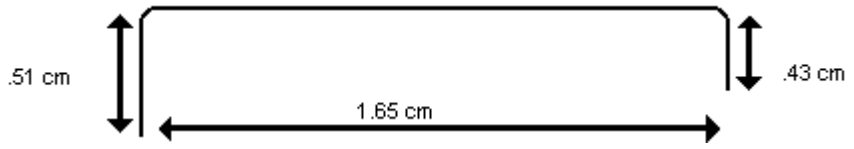


**Figure 1 (RE dimensions)**

**Working Electrode (WE)**

This is the center electrode used in electrochemistry and STM/CSAFM. This electrode doesn't require special cleaning because it is not in contact with the sample inside the liquid cell. An L-shaped pogo electrode may also be used.

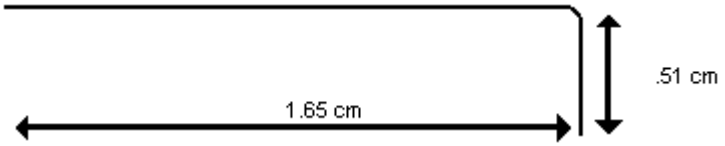


**Figure 2 (WE dimensions)**

**Counter Electrode (CE)**

Because of the large size of the liquid cell, the counter electrode should go around as much of the inner rim of the cell as possible. As such, its dimensions are more complex than those of the other electrodes. It may be useful to make the diameter of the electrode slightly larger than the diameter of the cell, so that the electrode holds itself in place within the cell. One type of wire to use is PtIr wire with a diameter of 0.25 mm (0.01").

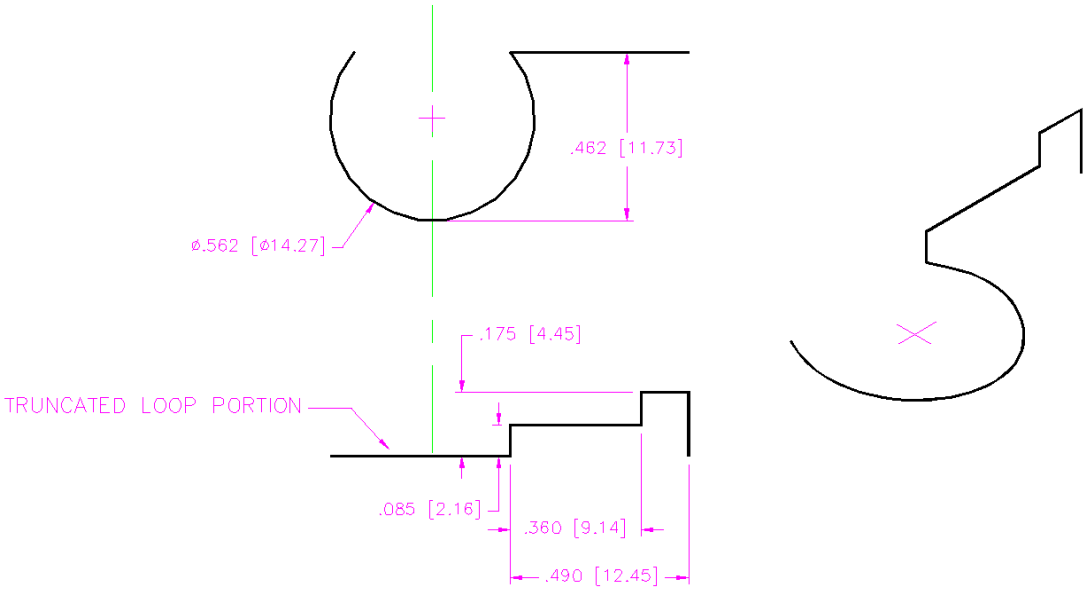


**Figure 3 (Counter electrode dimensions)**

## Substrate Preparation

If using gold substrates, they must be hydrogen flame annealed prior to imaging. For more information on annealing substrates, refer to the **PicoLE Hydrogen Flame Annealing Substrates** module. Gold substrates are available from Molecular Imaging, but they still must be annealed prior to use.

## Assembling and Loading the Liquid Cell

It is recommended that the assembly procedure be carried-out in a laminar flow hood or other clean environment.

1. Place a clean substrate onto the sample plate and push the cell onto the spring-loaded pins on the sample plate.

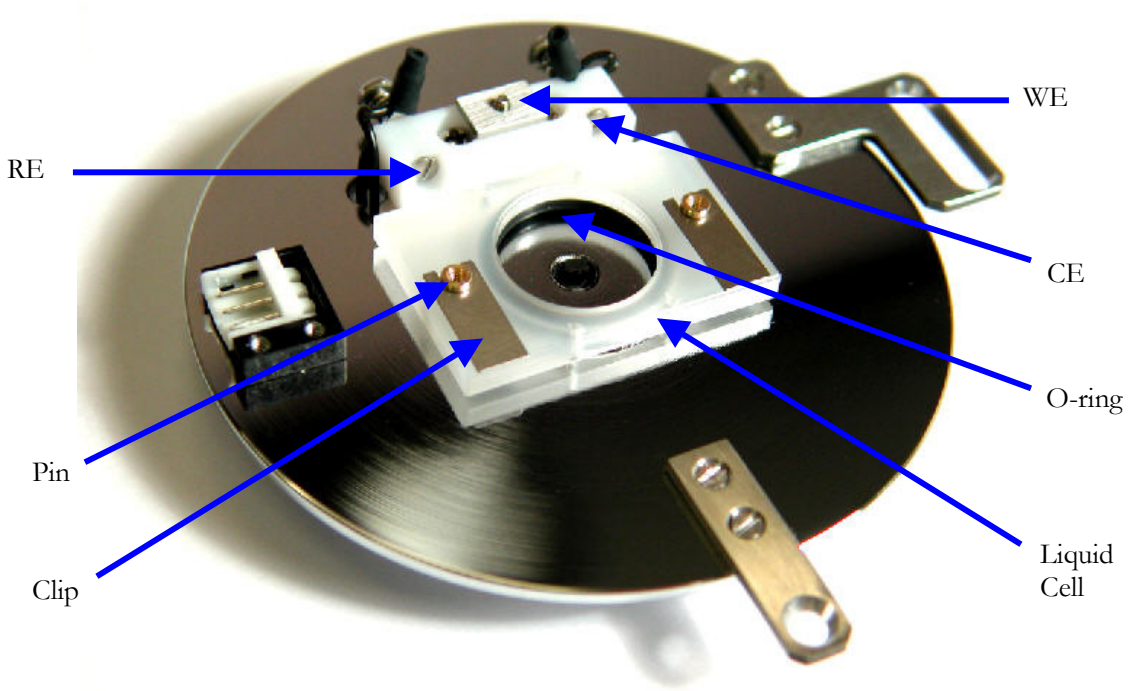


**Figure 4 (Sample stage with liquid cell in place.
Note: No electrodes are shown and there is no sample in place.)**

2. Pushing down, expose the pin slots (now pushing through the liquid cell plate) and insert the cell clamps.
3. Insert the counter and reference electrodes. Ensure that the electrodes will make good contact with the solution but do not touch the sample or each other. Due to the geometry of the liquid cell, the counter or reference wire passes underneath the working electrode wire.
4. Push the L-shaped working electrode contact into the hole in the wall of the cell nearest to the electrode clamping assembly on the sample plate.

5. Push up the working electrode clamp and place the end of the wire under the nut, letting the clamp spring back to clamp the electrode. Ensure that the working electrode is not touching the counter or reference electrode.

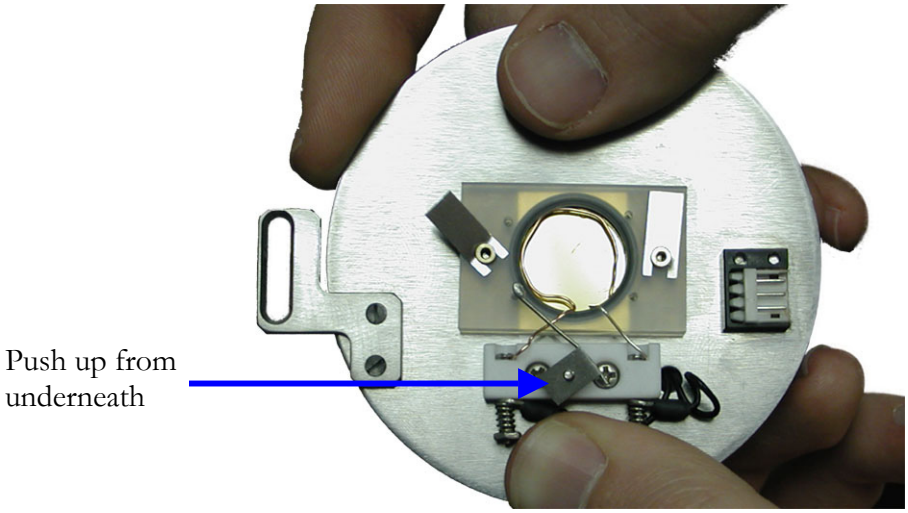


**Figure 5 (When released, the nut is pulled down holding the WE in place)**

6. Test that contact is established between the working electrode and the sample by inserting a wire into one of the three remaining holes in the Teflon cell and checking for continuity with a multimeter.
7. Check that both the reference and counter electrodes are making contact with the electrode clamping assembly on the sample plate with a multimeter.
8. Double check that the wires will clear the STM or AFM tip and will not touch any part of the underside of the microscope.

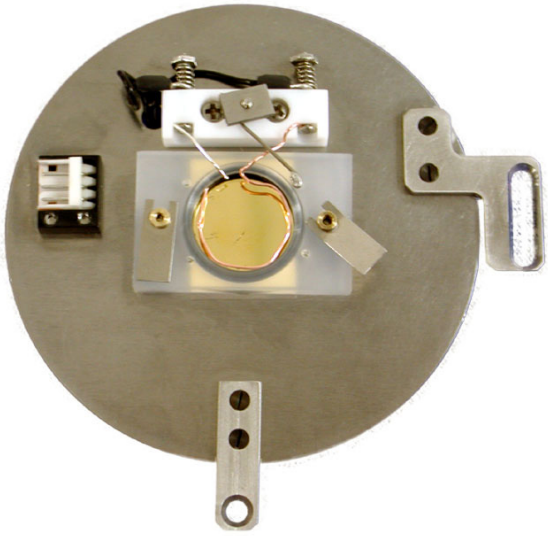

**Figure 6 (Sample stage with electrochemistry hardware in place)**

9. Fill the liquid cell.
10. Connect the sample plate to the microscope via the 3-pin EC cable.
11. Load the sample plate as outlined in the **PicoLE System module**.

## Software

1. Open the EC controls by selecting Electrochemistry from the **View** menu or clicking the 

button in the main toolbar. See **Chapter 3: Menu Bars** in the PicoScan software manual for more information.

2. See **Chapter 9: AFM Electrochemistry** of the PicoScan software manual for instructions regarding the electrochemistry controls.

## Quasi Reference Electrodes

Considerable simplification arises when a simple wire surface can be used as a reference electrode in the SPM liquid cell. It is extraordinarily difficult to prevent residual contamination from the ions needed to operate many of the standard reference electrodes. There are no simple rules to guide the choice of ions and wires used to establish a reference. Silver wire appears to be a good choice in many situations. Its reproducibility is often enhanced by oxidizing the wire in a solution of the electrolyte to be used in the experiment. The stability, reproducibility, and calibration all have to be established by suitable experiments.

### Stability

We recommend running cyclic voltammetry in the conditions to be used in the SPM experiment using the appropriate liquid cell. Check that features in the voltammogram do not move noticeably over the lifetime of a typical experiment.

### Reproducibility

This appears to be the major drawback of quasi reference electrodes. Their potential against a standard can vary considerably from wire to wire. It is essential to calibrate each wire before and after each experiment.

### Calibration

This is, in principle, a simple procedure. Measure the potential difference between the quasi reference and a standard reference electrode using, for example, the mV measuring input on a good pH meter while both are immersed in the electrolyte solution being used in the experiment. However, contamination of the quasi reference by, for example, chloride, can cause the calibration to drift. So, it is important to establish conditions that are as clean as those used in the SPM cell. We have found it very useful to use a salt bridge to slow diffusion of chloride from a standard Ag/AgCl/KCl reference. Two containers are used, one for each electrode. Each contains the electrolyte of interest, but the one containing the reference is contaminated. The two are coupled by an inverted U-tube containing the salt for which both anion and cation have equal mobilities (minimizing potential drop across the bridge). The ends of the bridge are sealed with plugs that slow diffusion of electrolyte across the bridge.

## Making a Salt Bridge

Equipment

- Pyrex Tube (inner diameter is approximately 3 mm)
- 100 mM $KBrO_3$
- Filter paper
- Bunsen burner

Procedure

1. Heat the tube over the burner and bend the ends so that you have a C-shaped tube.
2. Fill the tube with the 100 mM $KBrO_3$ and soak the filter paper in the same solution.
3. Stuff the ends of the tube with the pieces of the filter paper, making sure that there is no air left in the tube.
4. The bridge is placed between the working solution and the KCl solution.
5. Be sure to add water to the KCl solution as it evaporates.

After using the salt bridge, rinse the salt bridge thoroughly to remove any Cl. Store the bridge in the 100 mM $KBrO_3$ solution in a refrigerator covered (~ 5 °C). Make sure the reference end is stored in the reference solution. When reusing the salt bridge, be sure to rinse it thoroughly to prevent $KBrO_3$ contamination and replace the working solution each time.

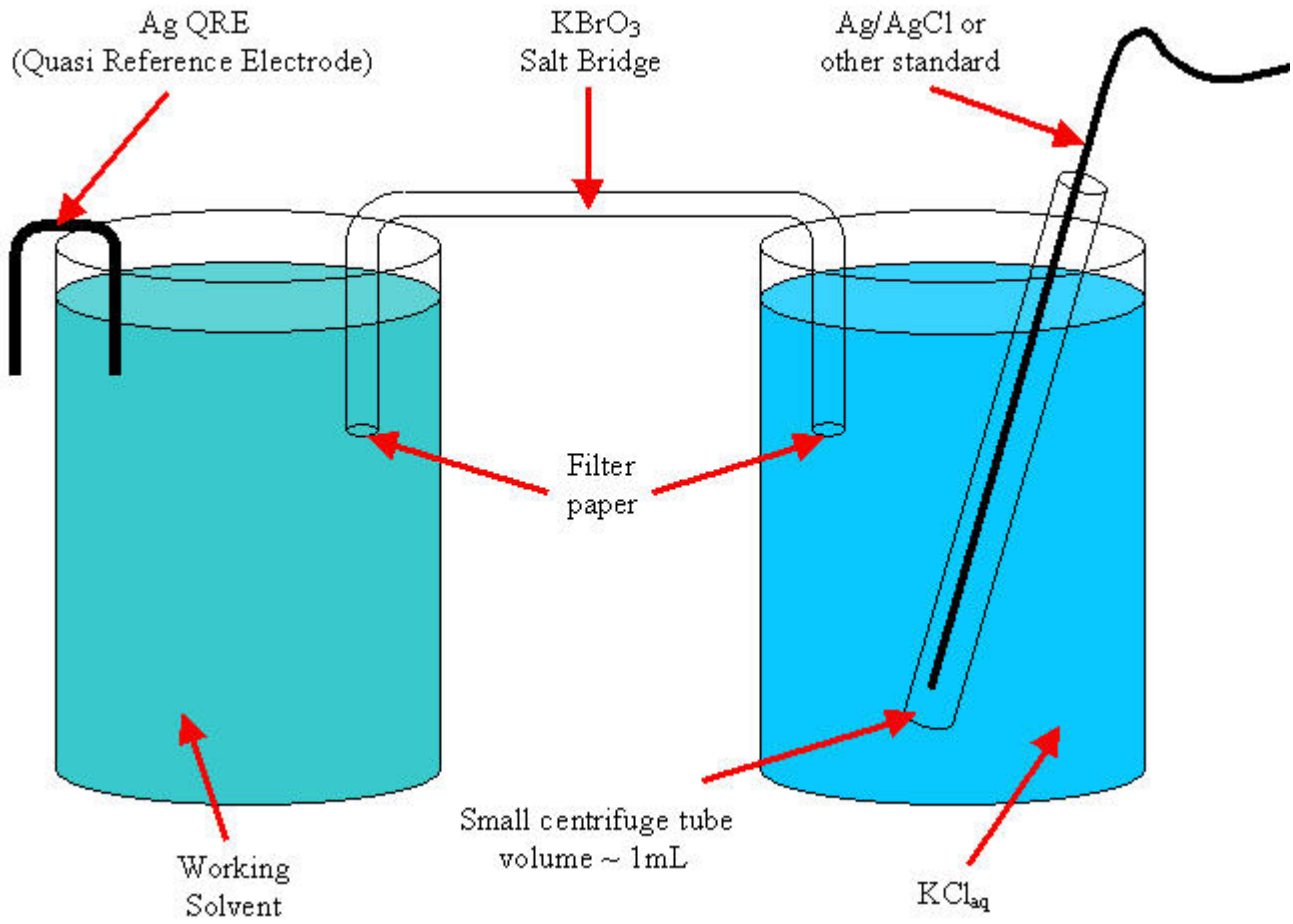


**Figure 1 (Salt Bridge diagram)**

## Troubleshooting

The most frequently encountered problem is leakage from around the bottom of the cell. It is generally more of a problem with solvents that "wet" the substrate well (like methanol). This causes leakage current and very erratic imaging. Carefully inspect for signs of leakage. If you find leakage, make sure that the sample is flat and large enough to fit underneath the liquid cell without gaps. Check that the O-ring is clean. Also, tightening the sample plate screws will increase pressure on the cell. If you still experience leakage, contact Molecular Imaging for further assistance.