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Running Rotating Ring-Disk Electrode (RRDE) Experiments with Squidstat Potentiostats

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RRDE is commonly used to study many types of convective electrochemical systems. This application note explains how to successfully carry out RRDE measurements with Squidstat potentiostats.

The two most common electrochemical systems involving forced convection, also known as hydrodynamic methods, are the *rotating disk electrode* (RDE) and the *rotating ring-disk electrode* (RRDE). Hydrodynamic methods are typically employed to investigate reaction mechanisms and simulate systems under convective mass transport. It can also be used to study reactions with slow current-limiting kinetics, which can have poor resolution in standard unstirred measurements. The most common application of RRDE is the study of oxygen reduction reactions.

In RDE, the rotation of the disk induces a flux of the electrolyte to the surface of the electrode, where the rate of flow is controlled by the angular velocity (ω) of the disk. Reaction kinetics and the effects of mass transport are investigated by steady-state voltammetry on the disk at different ω. However, the flux at the surface of the disk does not allow for reversal methods; the products of surface reactions are swept away from the rotating disk, so a reversal scan would produce the same i-V curve as the forward scan. In RRDE, a stationary ring electrode is placed around the rotating disk electrode to allow for reversal techniques such as cyclic voltammetry. Species generated at the disk electrode are swept toward and detected by the ring electrode, so the data collected at the ring provides information about the reactions occurring on the surface of the disk. Alternatively, the ring can be used to study the still solution when the disk is not rotating.

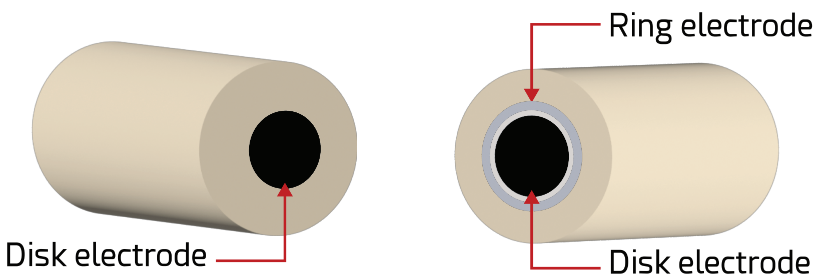


Figure 1. *A Rotating Disk Electrode (RDE, left) and a Rotating Ring-Disk Electrode (RRDE, right). Typically, the disk electrode is made of an inert material such as glassy carbon while the ring electrode is made of platinum.*

Connecting the Leads

A RDE cell uses a standard 3-electrode configuration consisting of the working electrode disk, a counter electrode, and a reference electrode. An RRDE cell uses a less common 4-electrode configuration consisting of two independent working electrodes. The primary working electrode (**WE 1**) is the disk while the secondary working electrode is the ring (**WE 2**). Both working electrodes share a common counter electrode (**CE**) and reference electrode (**RE**).

Since there are two working electrodes that must be independently controlled, a bipotentiostat is required to run RRDE experiments. Two Squidstat potentiostats can be configured to run in bipotentiostat mode. The following diagram illustrates the cable lead connections necessary to run RRDE:

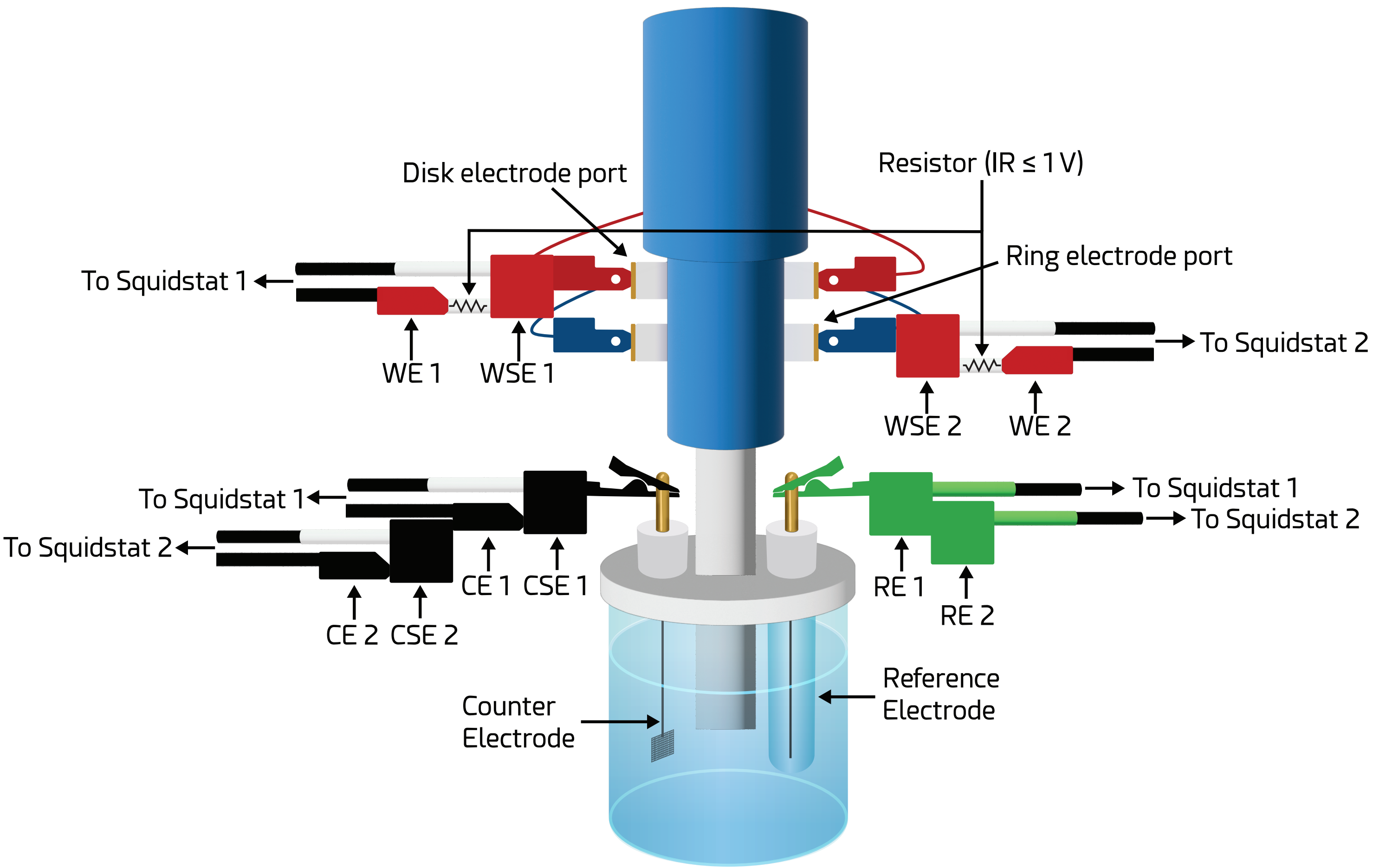


Figure 2. *Diagram of RRDE setup using two Squidstats in a bipotentiostat configuration. The counter (CE) and counter sense leads (CSE) from both Squidstats are stacked and connected to the common counter electrode, while the reference leads (RE) from both Squidstats are stacked and connected to the common reference electrode. The working (WE) and working sense leads (WSE) from Squidstat 1 are stacked and connected to the disk electrode, while the WE/WSE leads from Squidstat 2 are connected to the ring electrode. A resistor is placed between the WE and the WSE to reduce noise caused by AC ground loops. The reasons for the additional resistor connections are explained in the following section of this application note. Although any resistor of appropriate value is suitable to use for the RRDE measurement, custom resistor accessory pieces with built-in banana pins for easy cable connections are available from Admiral Instruments.*

Grounding Considerations for RRDE

When a device is grounded, it is connected to an infinite source or sink of charge. The most common ground is the planet Earth, aptly named "Earth ground." The primary reason for grounding is safety: grounding provides a path for excess current in the case of an overvoltage event and reduces the buildup of electrostatic charge. The secondary reason for grounding is to define a zero-voltage reference point, which gives us the basis to express voltage potentials relative to ground. All Squidstat potentiostats can be configured to run in two grounding modes, ground and float, via a switch on the back panel of the instrument. In ground mode, the working electrode is Earth grounded, while in float mode, the working electrode is connected to an internal ground.

In the bipotentiostat configuration required for RRDE, both Squidstats are electrically connected through the electrochemical device under test (DUT) and through the common Earth ground via a power source, most often a common electrical outlet. In this configuration, current now has multiple pathways to ground, forming a conductive ground loop. The flow of current through this loop can cause a voltage drop, altering the zero-reference point and resulting in unstable and inaccurate voltage measurements. The conductive ground loop issue can be resolved simply by setting both Squidstat channels to "float" mode using the switch located on the back panel of each instrument.

Although switching both Squidstats to float mode will prevent DC ground loops from forming, AC ground loops may form, resulting in oscillations and unstable data. The addition of an isolation resistor between the WE and the WSE leads for both the ring and the disk electrodes will negate the effects of an AC ground loop by reducing the magnitude of the loop current. The value of the resistor should result in a voltage drop less than or equal to 1 V, calculated from the maximum expected current using Ohms law (V = IR). For example, if the maximum expected current is 1 mA, the resistor should be 1 kOhm or less:

$$IR = V \longrightarrow IR \leq 1\ \text{V} \longrightarrow R \leq \frac{1\ \text{V}}{1\ \text{mA}} \longrightarrow R \leq 1\ \text{kOhm}$$

The compliance voltage of the potentiostat - that is the maximum voltage which can be supplied to the counter electrode to control the potential at the working electrode - is reduced by the value of the voltage drop across this resistor. The Squidstat Plus has a compliance voltage rating of 12 V. If the correct resistor is used, the compliance voltage will only be reduced to 11 V. However, if a higher resistance is used and the voltage drop exceeds 1 V, the compliance voltage will be significantly reduced and the potentiostat may not be able to apply the correct potential to the working electrode. Therefore, this value should be calculated for both the ring and disk working electrodes separately to ensure that the voltage drop across the resistor is below 1 V for each electrode.

Running an RRDE Experiment in the Squidstat User Interface

In a typical RRDE experiment, the ring electrode is set at a fixed voltage bias with respect to the reference electrode or open circuit (Chronoamperometry), while the disk is subjected to a steady-state potential scan between two potential limits (Cyclic Voltammetry). The potential waveform applied by the potentiostat is shown in Figure 3. Currents measured at the disk and the ring are plotted against the potential of the disk electrode.

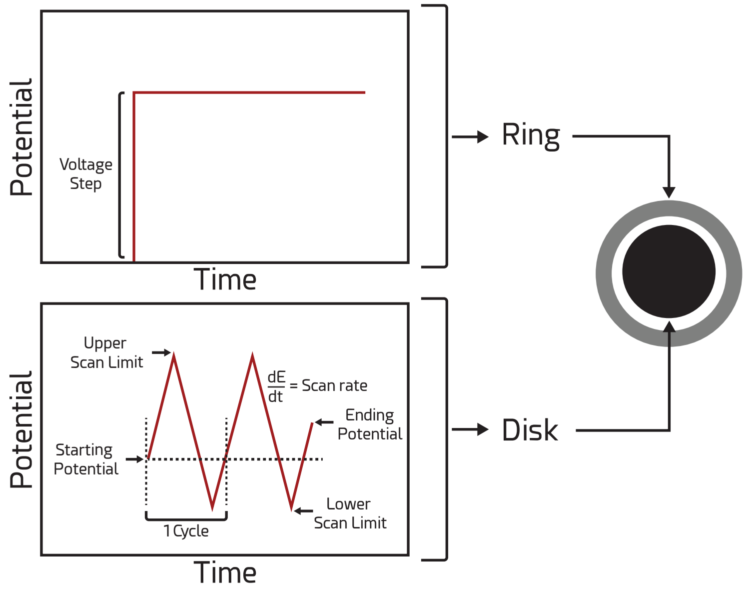


Figure 3. *Potential waveforms applied to the ring electrode and the disk electrode for the pre-built RRDE experiment in the SUI. The potential of the disk electrode is swept back and forth between the upper scan limit and the lower scan limit at a constant scan rate (dE/dt) for a specified number of cycles. A user can select to scan to the lower scan limit or the upper scan limit first. The cycling scheme is as follows: Starting potential -> [Scan limit 1 -> Scan limit 2]n -> Ending potential, where "n" is the number of cycles. The ring electrode is at a fixed potential with respect to the reference or open circuit.*

The pre-built RRDE experiment in the Squidstat User Interface (SUI) gives the user several options to customize their experiment, pictured on page 5. These parameters are described below.

Disk Parameters:

Disk instrument: Select which Squidstat is being used to control the disk.

Disk channel: Select the channel on the Squidstat which will control the disk. In cases where a single-channel Squidstat is assigned, this will default to Channel 1.

Cycles: The number of cycles to be performed. The cycling scheme is as follows: Starting potential → [Scan limit 1 → Scan limit 2]n → Ending potential, where "n" is the number of cycles.

Start new .csv file for each cycle: Choose "Yes" to create one .CSV file per cycle or "No" to create one .CSV file for all cycles.

Quiet time: The starting potential of the disk and the ring potential will be applied for the length of time input here before the scanning portion of the RRDE experiment begins.

Quiet time sampling interval: The time difference between two consecutive data points during the "Quiet Time."

Starting potential: The potential that is applied to the disk at the start of the scan.

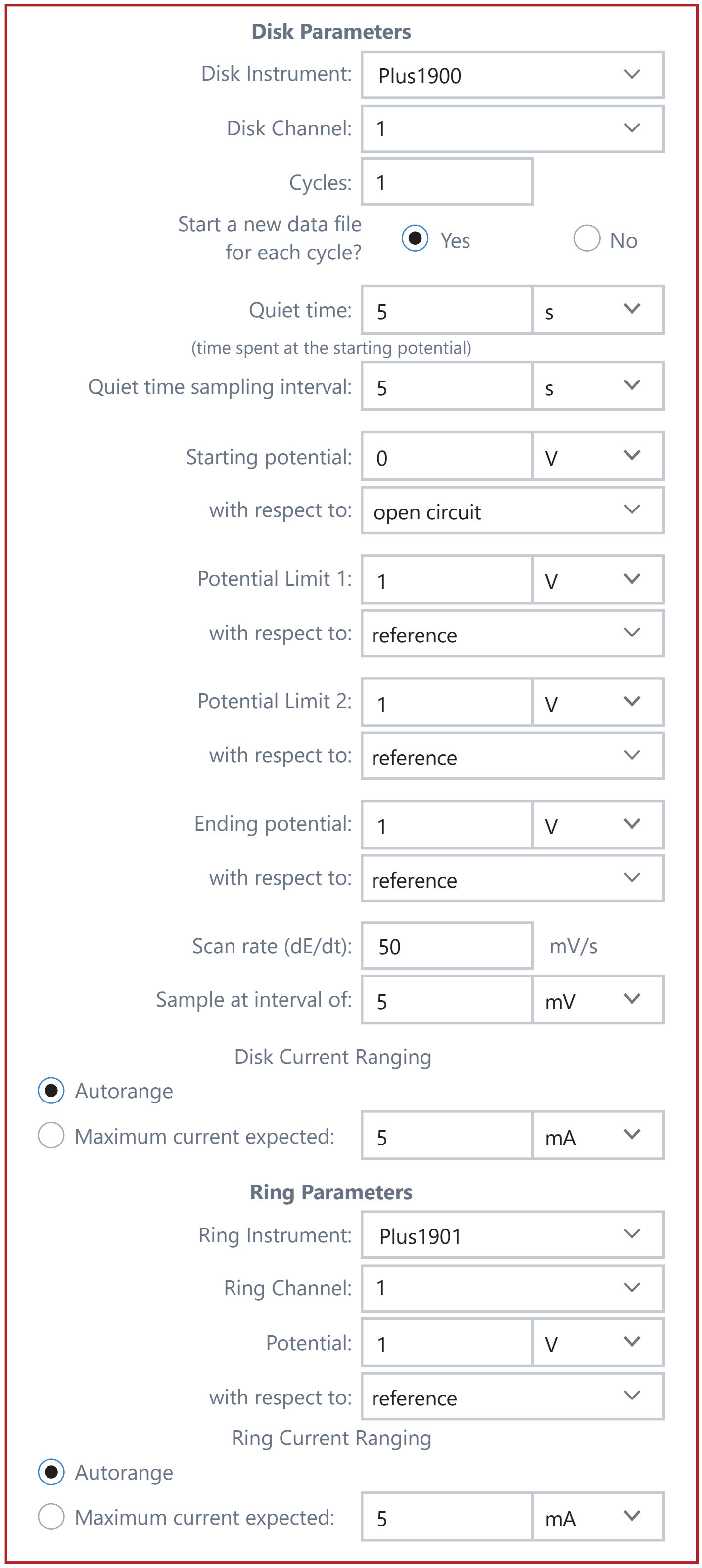
With respect to: The relative potentials against which the working electrode potentials are set. Users can select either "open circuit" or "reference." Reference refers to the potential of the electrode where the reference electrode lead is attached. Open circuit refers to the open circuit potential, which is the potential of the working electrode (relative to the reference electrode) when there is no flow of current. For an RRDE experiment it is recommended that all potentials are set with respect to reference.

Potential Limit 1: The initial potential limit which the potentiostat will scan to from the Starting Potential. This value can be either more positive or more negative than the starting potential.

Ending potential: The scan will end at this potential.

Potential Limit 2: The second potential limit which the potentiostat will scan to from Potential Limit 1.

Scan rate: The rate of change of the disk potential with respect to time.



Sample at intervals of: The interval between two consecutive current data points. It can be set based on an interval of time (ms/s/min/hr) or potential (mV).

Disk current ranging: More than one current range exists in Squidstats to measure a wide scale of current magnitudes accurately. Although the user can let the SUI choose the current range corresponding to the magnitude of the current response (Autorange), in some cases this will result in noise and loss of data. Therefore, options are provided for Autorange and fixed range modes.

Autorange: This is the default setting. The best current range for the highest achievable accuracy is automatically selected, and in cases where multiple current ranges must be used, the Squidstat will automatically switch to different current ranges.

Maximum current expected: Select the desired current range by entering a maximum current value. This is useful to avoid noise created when the Squidstat switches between current ranges.

Ring Parameters:

Ring instrument: Select which Squidstat is being used to control the ring.

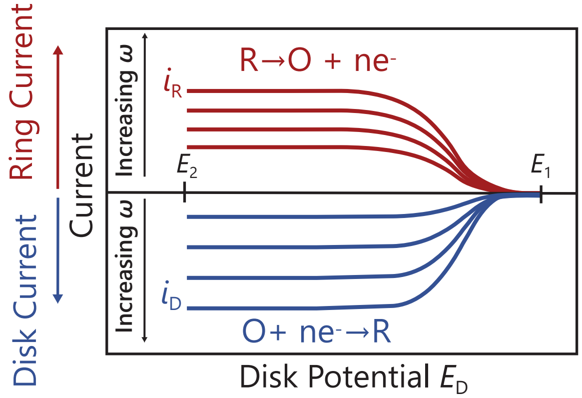
Ring channel: Select the channel on the Squidstat which will control the disk. In cases where a single-channel Squidstat is assigned, this will default to Channel 1.

Potential: This is the constant potential that is applied at the ring electrode.

Ring current ranging: The same concept as disk current ranging explained above.

Example

Consider an ideal experiment with a completely reversible redox couple with a reduction potential $E_{1/2}$ where the reaction rates are only limited by mass transport. The potential of the disk is scanned between two potentials E_1 and E_2, where the starting potential E_1 is a potential well positive of $E_{1/2}$ where no current is flowing, and E_2 is a potential negative of $E_{1/2}$. As the potential of the disk moves from E_1 to E_2, a cathodic current is observed resulting from the reduction of species O according the reaction $O + ne^- \rightarrow R$. Since the disk is rotating at an angular velocity ω, species R is transported radially away from the disk toward the ring electrode. The ring is held at an oxidizing potential E_R such that when species R reaches the ring, it is oxidized back to species O by the reverse reaction $R \rightarrow O + ne^-$, resulting in an observed anodic current. The experiment is repeated for different values of ω, and the resulting current profile at the disk (i_D) and the ring (i_R) is plotted as a function of the disk potential E_D. A theoretical ideal voltammogram for this RRDE example is given in **Figure 4**.



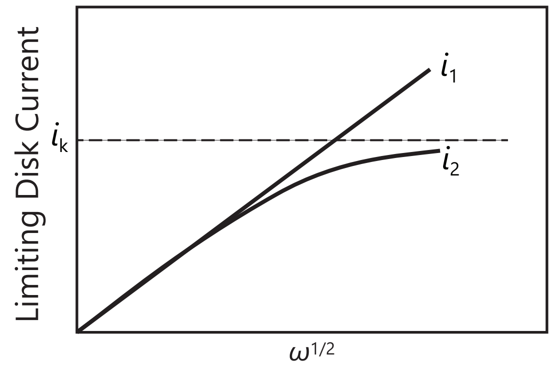


***Figure 4**. Simulated voltammograms from an RRDE experiment at various rotation rates (ω)[**Left**]. The potential of the disk is cycled between two potentials E_1 and E_2 at a constant scan rate to reduce species O, while the ring is held at a constant potential E_R to oxidize species R. The current response at the disk i_D (blue) and at the ring i_R (red) is plotted as a function of the disk potential, E_D. A Levich plot of limiting disk current (i_D) vs. rotation rate ($\omega^{1/2}$) for an ideal reaction without kinetic limitations (i_1) and a reaction with slow kinetics (i_2)[**Right**]. For an ideal reaction, $i_D \propto \omega^{1/2}$. For a reaction with slow kinetics, i_D vs. $\omega^{1/2}$ approaches the kinetic limiting current i_k as $\omega^{1/2} \rightarrow \infty$.*

The shape of the voltammograms at the ring and the disk tells us information about the reaction mechanisms and kinetics (**Figure 4**). The voltammogram for an ideal reversible half-reaction without competing chemical reactions or kinetic limitations is sigmoidal with two flat current limiting regions. The initial plateau at the upper limit E_1 is the baseline current, which is theoretically 0 as no reactions are occurring in this potential region. The second plateau around the lower limit E_2 is the potential region where current is limited by mass transfer. The magnitude of the difference between the two current limiting plateaus gives the mass-transport limiting current for the ring (i_R) and the disk (i_D).

For the same ideal electrochemical system, the magnitude of i_D will increase linearly with the square root of ω. Thus, i_D is typically plotted as a function of $\omega^{1/2}$ on a graph named a Levich plot (**Figure 4**). This relationship should be linear and the line should pass through the origin. Deviations from this behavior indicate kinetic limitations. For a reaction with slow kinetics, i_D will approach the kinetic limiting current (i_k) as $\omega^{1/2} \rightarrow \infty$.

One of the most important parameters determined from an RRDE experiment is the collection efficiency, or what fraction of species R generated at the disk electrode reaches the ring electrode. This is determined from the ratio of i_R to i_D:

$$N = \frac{|n_R i_R|}{|n_D i_D|}$$

where N is the collection efficiency, and n_R and n_D are the number of electrons transferred at the ring and disk, respectively.

While the collection efficiency can be determined experimentally, it is an empirical property of the RRDE electrode. A higher collection efficiency is desired to maximize the current signal at the ring electrode. Decreasing the space between the disk and the ring is one way to increase the collection efficiency of the RRDE.

If species R is stable, *N* depends only on the electrode geometry and is independent of concentration, kinetics, ω, and i_D. Therefore, the value for *N* obtained from an experiment performed on a well-behaved system gives the empirical *N* for that RRDE and is valid for different experiments on that electrode. However, if R is not stable, it may decay into an intermediate species before reaching the ring, leading to a smaller N that *does* depend on concentration, kinetics, ω, and i_D. The rate constant for the decay of R can be estimated by comparing the experimental *N* to the empirical *N* for the given RRDE at different ω. A full analysis of this method and other analytical techniques for non-ideal systems is beyond the scope of this application note.

Summary

RDE and RRDE are hydrodynamic methods used to study reaction kinetics and mechanisms in a stirred solution. RDE uses a standard 3-electrode setup while RRDE requires a 4-electrode setup containing two independently controlled working electrodes, the ring and the disk. The addition of a ring electrode in RRDE allows for reversal techniques that cannot be performed using traditional RDE. Two Squidstat potentiostats can be used in a bipotentiostat configuration to run RRDE experiments using the pre-built experiment in the SUI. There are several factors to consider when running RRDE with Squidstats:

1. One Squidstat controls the disk working electrode while the other Squidstat controls the ring working electrode. Both instruments are connected to the common counter electrode and common reference electrode.
2. Set both Squidstats to “float” mode using the switch on the back of the instrument to avoid DC ground loops.
3. Place a resistor between the working and working sense leads to mitigate AC ground loops as shown in the photo below. The voltage drop across this resistor should be 1 V or less.

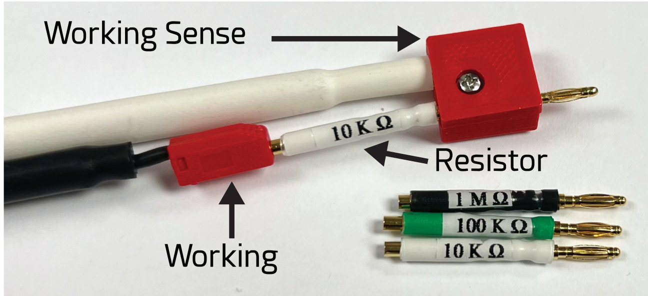


Figure 5*. Photo of a resistor placed between the working sense and working electrode leads to mitigate the formation of AC ground loops. Custom resistor accessory pieces with built-in banana pins for easy cable connections shown here are available from Admiral Instruments.*