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

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RRDE is commonly used to study electrocatalytic activity and many types of convective electrochemical systems. This application note explains how to successfully carry out RRDE measurements with two Squidstat potentiostats configured as a bipotentiostat.

The two most common electrochemical systems involving forced convection, or hydrodynamic methods, are those that actively stir a solution using a *rotating disk electrode* (RDE) or a *rotating ring-disk electrode* (RRDE). Hydrodynamic methods are employed to investigate reaction kinetics and mechanisms, as well as simulate systems under convective mass transport. They can also be used to study reactions with slow current-limiting kinetics, diagnose catalytic off-products, and define lifetimes of fast decaying intermediates. The most common application of RRDE is the study of oxygen reduction reactions by electrocatalysts employed in fuel cells.

In both RDE and RRDE, the rotation of the electrode in solution induces a flux of the electrolyte to the surface of the electrode, where the rate of flow is controlled by the angular velocity ($\boldsymbol{\omega}$) of the electrode. For RDE, reaction kinetics and the effects of mass transport are investigated at the rotating disk at different $\boldsymbol{\omega}$ by evaluating the limiting current i_{lim} versus the $\boldsymbol{\omega}^{1/2}$ (Levich analysis) or i_{lim}^{-1} versus $\boldsymbol{\omega}^{-1/2}$ (Koutecky-Levich analysis). Among other things, the Levich analysis can provide values for diffusional coefficients and rate constants. Kinetic limitations are evaluated using the Koutecky-Levich analysis as the line of best fit will go through 0 for all systems that do not display sluggish kinetics. Electrocatalysts can also be immobilized at a disk to study mechanistic and kinetic information by supplying a substrate to the solution and performing a desired voltammogram (i.e. cyclic voltammetry, or linear sweep), thereby eliminating diffusional properties of the catalyst and minimizing those of the substrate.

In RRDE, a ring electrode is placed around the disk electrode. Experiments involving RRDE can provide identical information as RDE but with increased information as the ring is poised at a sufficient potential to allow for detection of specific products diffusing outward from the disk. Increasing $\boldsymbol{\omega}$ decreases the time a molecule will take to diffuse to the ring. This enables the ring to provide information about reaction mechanisms and kinetics resulting from interactions occuring at the surface of the disk.

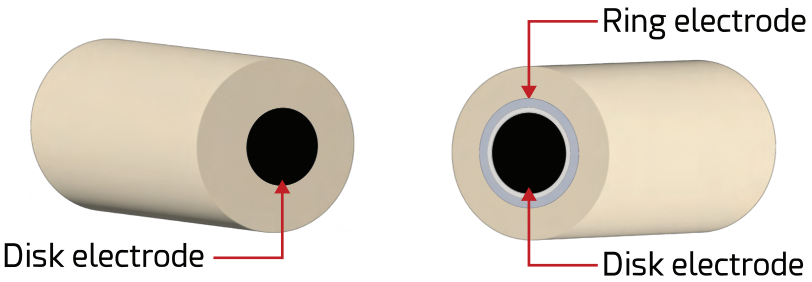


Figure 1. *A Rotating Disk Electrode (RDE, left) and a Rotating Ring-Disk Electrode (RRDE, right). Typically, the disk electrode is made of an inert material such as glassy carbon while the ring electrode is made of platinum or gold.*

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 experiments, both Squidstats are electrically connected through the electrochemical device under test 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. **For bipotentiostat mode to perform properly, both Squidstats must be in "float" mode.**

Determining the Theoretical Collection Efficiency for your RRDE

The observed collection efficiency is an inherent and fundamental property of the rotating ring-disk electrode geometry that is employed in any experiment and is dependent upon three key parameters: 1) disk electrode geometrical area, 2) ring electrode geometrical area, and 3) the non-electroactive space bewteen the ring and the disk electrodes. This relationship was first proposed in 1966 by Albery and Bruckenstrein. An intuitive and helpful interactive example of this relationship can be found from WOLFRAM Demonstation projects. Figure 2 provides a brief overview. A final important consideration is the acceptable rotational rates for a given RRDE which should be provided by the manufucter. Rotational rates above a specified value may lead to reduced collection effieincy and inaccurate data collection.

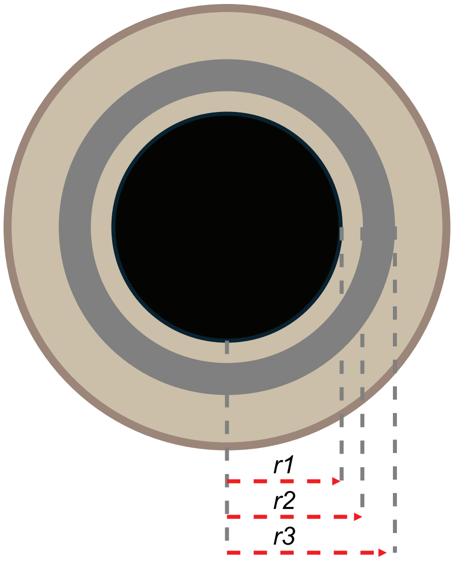


Figure 2. *Import radii for calculating the theoretical collection efficiency for a rotating ring-disk electrode. It is important to conduct control experiments and verify you are indeed acheiving values close to theoretical values.*

Connecting the Leads

An RDE cell uses a standard 3-electrode configuration: working electrode (disk), counter electrode, and reference electrode. An RRDE cell uses a less common 4-electrode configuration consisting of two independent working electrodes. In our example below, the primary working electrode (**WE 1**) is the disk while the secondary working electrode is the ring (**WE 2**). Both working electrodes are independently controlled and share a common counter electrode (**CE**) and reference electrode (**RE**). A bipotentiostat is then generally required to facilitate RRDE experiments. However, two Squidstat potentiostats can be configured to enable bipotentiostat mode. Figure 3 illustrates the cable lead connections necessary to complete RRDE experiments using two Squidstats in bipotentiostat mode.

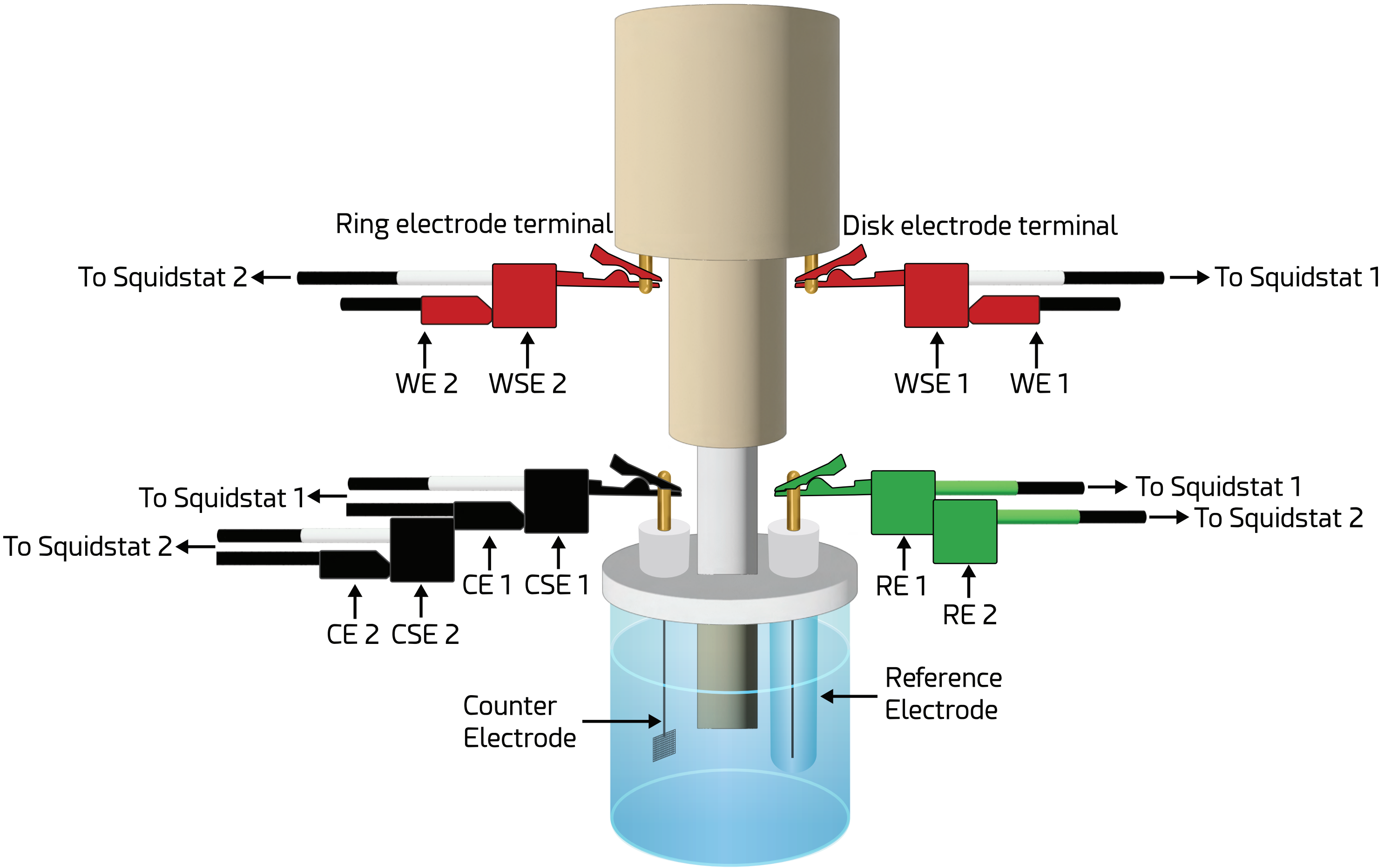


Figure 3. *Diagram of an RRDE setup using two Squidstats in a bipotentiostat configuration. An RRDE electrode has already been equipped and the shaft lowered into solution, while keeping the interface of the electrode at the shaft above the solution. The counter (CE) and counter sense (CSE) leads from both Squidstats are stacked and connected to the common counter electrode, while the reference (RE) leads from both Squidstats are stacked and connected to the common reference electrode. In this illustration, the working (WE) and working sense (WSE) leads 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.*

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 or Linear Potential Sweep Voltammetry). The potential waveform applied by the potentiostat is shown in Figure 4 for cyclic voltammetry and chronoamperometry. Currents measured at the disk and the ring are plotted against the potential of the disk electrode.

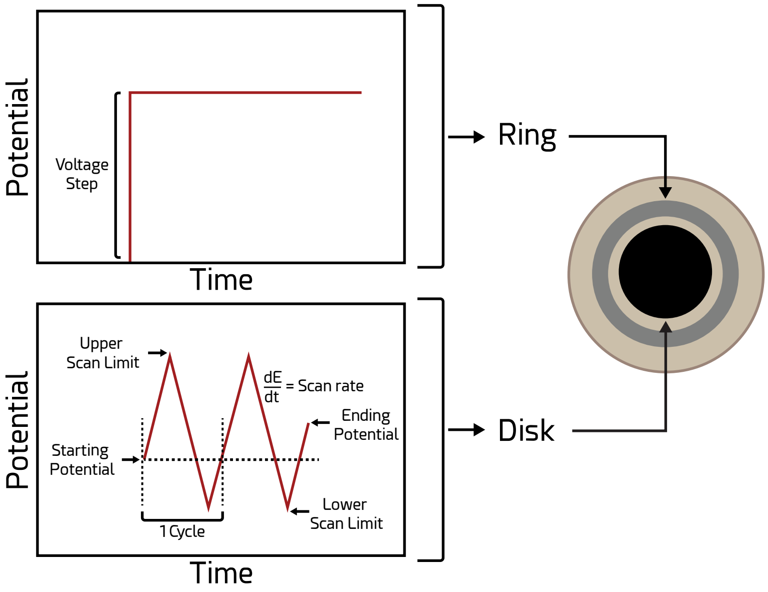


Figure 4. *Potential waveforms applied to the ring electrode and the disk electrode for the pre-built RRDE experiment in the SUI. The potential of the disk electrode is swept back and forth between the upper scan limit and the lower scan limit at a constant scan rate (dE/dt) for a specified number of 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 and is depicted 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: Number of cycles to be performed. Cycling scheme, where "n" is number of cycles, is as follows: Starting potential → [Scan limit 1 → Scan limit 2]n → Ending potential

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

Quiet time: The starting potential of the disk and the ring 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.

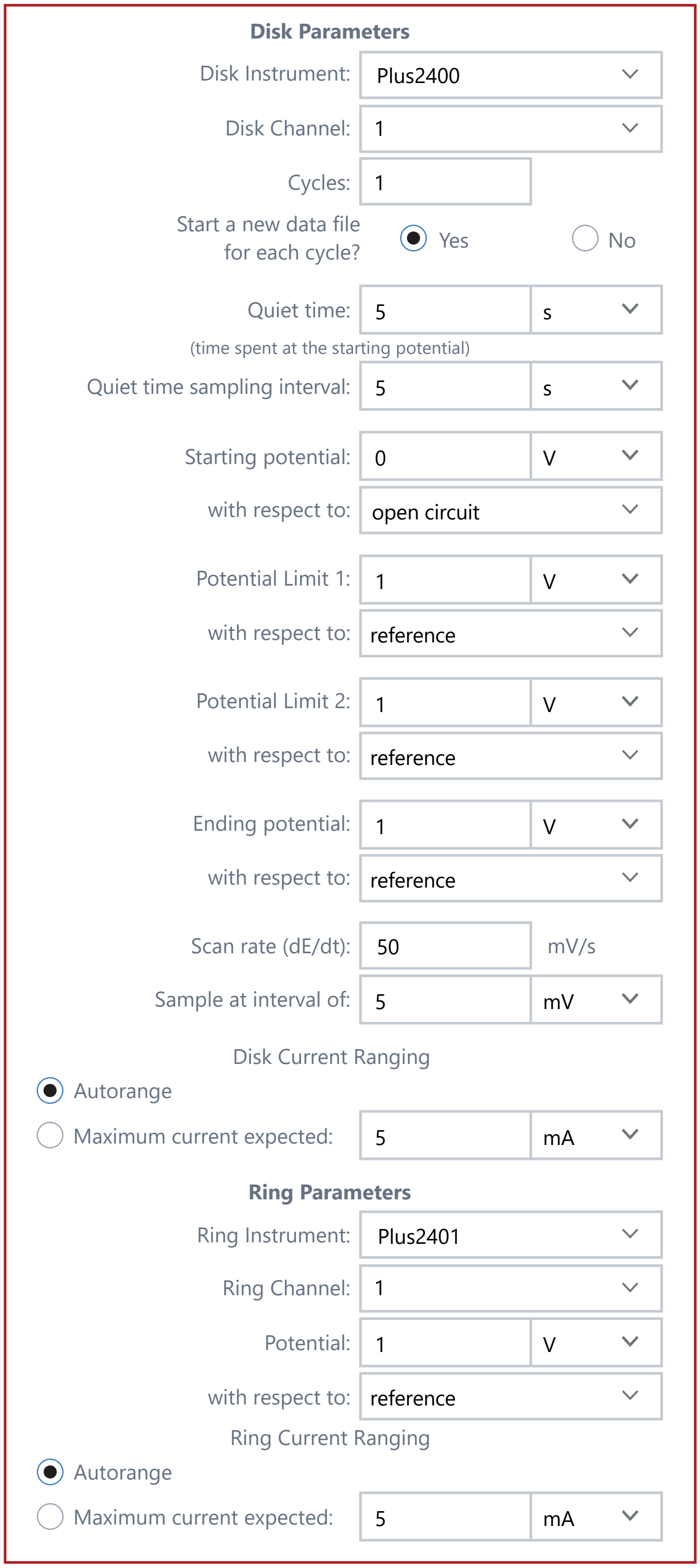
With respect to: The relative potentials against which the disk electrode potentials are set. Users can select either "open circuit" or "reference." Reference refers to the potential of the electrode where the reference electrode lead is attached. Open circuit refers to the open circuit potential, which 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.

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

Ending potential: The scan will end at this potential.

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



Disk Parameters
Disk Instrument: Plus2400
Disk Channel: 1
Cycles: 1
Start a new data file for each cycle? ● Yes ○ No
Quiet time: 5 s
(time spent at the starting potential)
Quiet time sampling interval: 5 s
Starting potential: 0 V
with respect to: open circuit
Potential Limit 1: 1 V
with respect to: reference
Potential Limit 2: 1 V
with respect to: reference
Ending potential: 1 V
with respect to: reference
Scan rate (dE/dt): 50 mV/s
Sample at interval of: 5 mV
Disk Current Ranging
● Autorange
○ Maximum current expected: 5 mA
Ring Parameters
Ring Instrument: Plus2401
Ring Channel: 1
Potential: 1 V
with respect to: reference
Ring Current Ranging
● Autorange
○ Maximum current expected: 5 mA

Sample at interval of: The interval between two consecutive current data points. 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 dynamically selected, and in cases where multiple current ranges will be spanned, 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 Squidstat channel to control the ring. 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 where a completely reversible redox couple displays a reduction potential ($E_{1/2}$) that shows reaction rates which are only limited by mass transport. The potential of the disk is scanned between a starting potential (E_1) sufficiently positive of $E_{1/2}$ where no faradaic current is observed and an ending potential (E_2) sufficiently more negative than $E_{1/2}$. 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. If species R reaches the ring, it is oxidized back to species O as the ring is maintained sufficiently more positive than $E_{1/2}$ and quite possibly E_1. An anodic current is observed at the ring from the reverse reaction $R \rightarrow O + ne^-$. This experiment is repeated for different values of ω. The raw current profiles at the disk (i_D) and the ring (i_R) can be plotted as a function of the disk potential (E_D). Data collected using two Squidstat Plus potentiostats in a bipotentiostat configuration is shown in Figure 5.

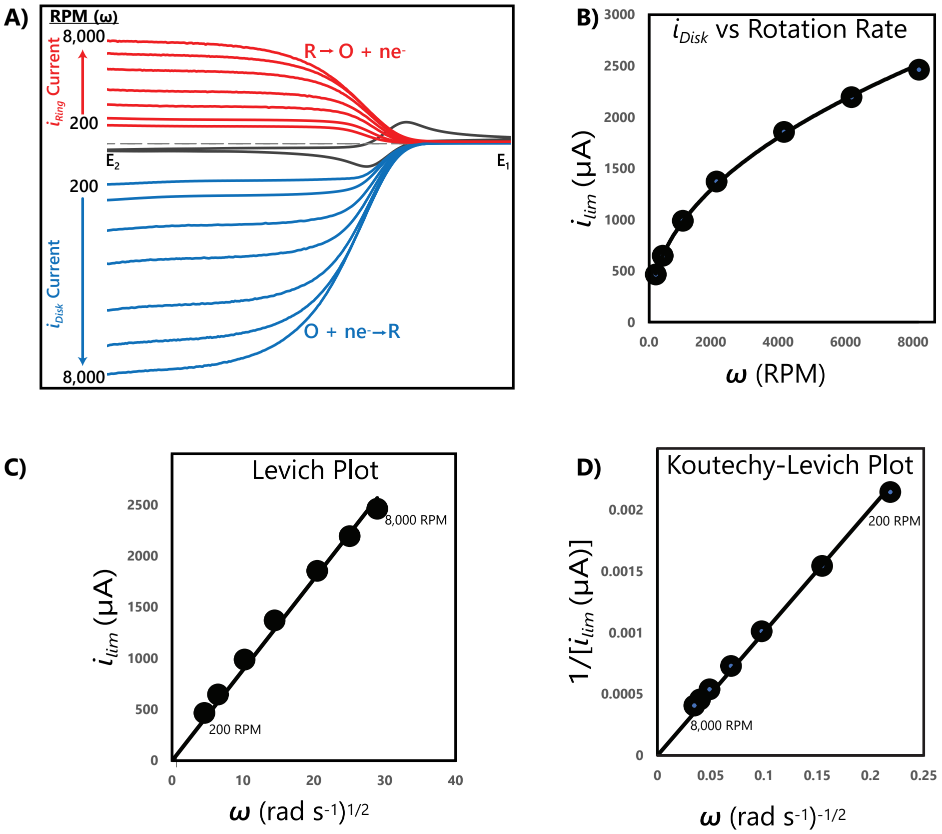


***Figure 5**. A) Experimental data collected using two Squidstat Plus potentiostats as a bipotentiostat using an RRDE-3A rotator equipped with an RRDE containing a glassy carbon disk and a platinum ring in the presence of 10 mM K[Fe(CN)$_6$] in an aqueous solution containing 0.1 M KCl. The experiment was started at +0.7 V, followed by scanning in the cathodic direction at 50 mV s^{-1} to an ending potential of -0.8 V. Disk data is shown in blue and ring data in red. The response from the disk with **ω** = 0 is shown in grey and the zero y-axis is shown as a dashed line. B) i_{lim} vs rotational rate shows a non-linear response as **ω** is increased. C) Levich plot shows a linear response from 200 to 8000 rpm. D) Koutechy-Levich plot shows a linear dependence from 200 to 8000 rpm with a y-intercept through 0.*

Practical Uses of Collection Efficiency

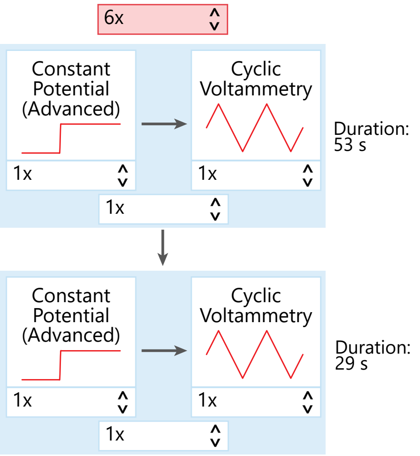
Determination of collection efficiency from an RRDE experiment is an important parameter to elucidate to provide confidence in the quality of the data being collected. Collection efficiency is the fraction of species R, generated at the disk electrode, that reaches the ring electrode and is further oxidized back to species O. Calculations use the absolute value of the ratio of i_R to i_D at a potential sufficient for i_{lim} conditions:

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

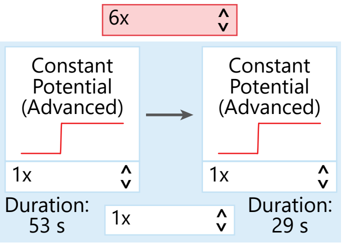
where N is the collection efficiency (CE), and n_R and n_D are the number of electrons transferred at the ring and disk, respectively. If species R is stable, N depends only on the electrode geometry and is independent of concentration, kinetics, **ω**, and i_D at i_{lim} conditions. Therefore, the value for N obtained from an experiment performed on a well-behaved system gives the empirical N for that RRDE geometry and is valid for different experiments using that electrode. However, if R is not stable, it may decay into an intermediate species before reaching the ring, leading to a decreased N that *does* depend on concentration, kinetics, **ω**, or i_D at i_{lim}. 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**. Decaying N at higher rotational rates can also be attributed to an RRDE electrode failing due to a **ω** incompatible with the electrode design. A full analysis of this method and other analytical techniques for non-ideal systems is beyond the scope of this application note.

Advanced RRDE Experiments Employing a Third Squidstat To Control Rotator Speed

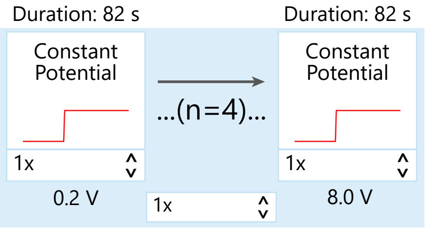
Three custom experiments can be constructed to simultaneously control the disk electrode, ring electrode, and rotator speed to enable an automated detailed interrogation of the electrochemical species in solution.



Constant Potential (Advanced) tile before a ***Cyclic Voltammetry*** (or ***Linear Potential Sweep***) tile enables quiet time. The potential window and scan rate provide the time course. ex. 1200 mV window @ 50 mV s^{-1} *dE/dt* = 24 s. Multiple sets of tile groups as shown to the left can be added to step from one scan rate to another. The dropdown box highlighted in red allows both tile groups to be repeated 6 times as the rotational speed is increased.

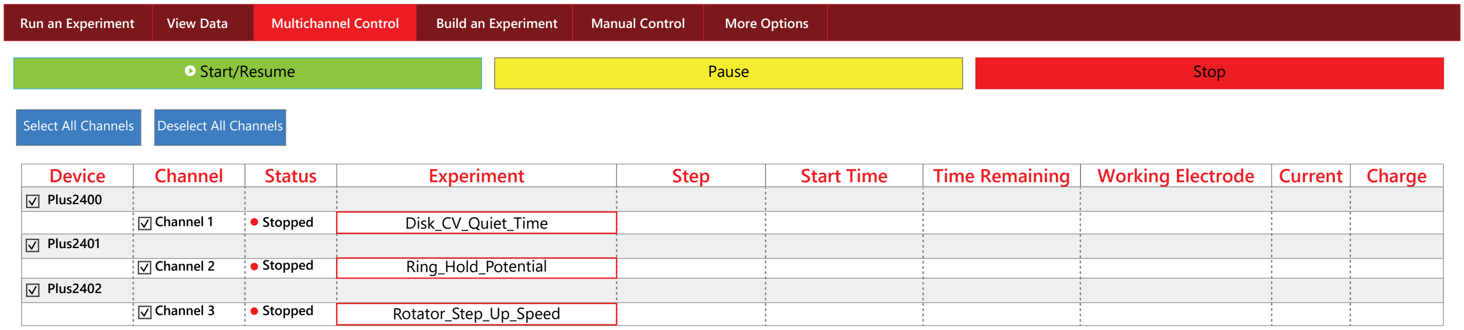


Constant potential (Advanced) tiles control the potential at the ring to facilitate converting products generated at the disk. The advanced tile disallows autoranging when a maximum expected current is input. Each constant potential experiment must have a duration equivalent to the quiet time plus the cyclic voltammogram. The repeat number must match as well.



Constant potential tiles control the rotational rate of the RRDE over the course of the experiment series. For RRDE-3A (1 V = 1000 RPM). Duration of these tiles = the sum of each constant potential experiment at the ring. Six voltage steps from 200 to 8000 RPM are completed using 6 constant potential tiles each with an increasing constant voltage and equivalent duration.

After building the custom experiments, use the "***Multichannel Control***" tab to load each experiment to the designated potentiostat, allowing all three to be initiated simultaneously. Click in the red box under "***Experiment***" to load. Click "***Select All Channels***", then click "***Start/Resume***" to begin data collection.



Device	Channel	Status	Experiment	Step	Start Time	Time Remaining	Working Electrode	Current	Charge
☑ Plus2400									
	☑ Channel 1	● Stopped	Disk_CV_Quiet_Time						
☑ Plus2401									
	☑ Channel 2	● Stopped	Ring_Hold_Potential						
☑ Plus2402									
	☑ Channel 3	● Stopped	Rotator_Step_Up_Speed						

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 or custom experiments can be developed to meet specific interrogations. 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. ***RRDE cannot be completed properly without completing this step***.
3. Employing the collection efficiency calculator (referenced below) and comparing to control reactions conducted in your lab will provide confidence that the data you are collecting is indeed of high quality.
4. Our “***Build an Experiment***” and “***Multichannel Control***” tabs can be utilized to efficiently define and execute advanced RRDE experiments that automate detailed multi-component experiments. This includes the ability to control the rotational rate of the RRDE via the Squidstat User Interface by connecting a third Squidstat potentiostat to the motor control system.
5. ***Sampling interval should be set to equivalent values for the ring and disk data during collection when using custom experiments to aid in plotting raw i_R and i_D vs E_D.***
6. Autorange should not be activated for any RRDE experiments for either the ring or the disk. Instead, set a maximum expected current to disallow current range switching during RRDE experiments.
7. Squidstat Cyclers cannot be used at the ring or the disk for RRDE experiment. Squidstat Cyclers can be used in advanced RRDE setups when controlling the rotational speed of the motor.

References

1. RRDE Interactive Collection Efficiency Calculator: https://demonstrations.wolfram.com/CollectionEfficiencyOfARotatingRingDiskElectrode/
2. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., New York: Wiley, 2001.
3. W. J. Albery and S. Bruckenstein, "Ring-Disc Electrodes. Part 6.—Second-Order Reactions," Transactions of the Faraday Society, 62, 1966 pp. 2584–2595. doi:10.1039/TF9666202584.