RDE-2

June 2000

Part MF-9006 **INSTRUCTION MANUAL**

Rotating Disk Electrode

Bioanalytical
Systems, Inc.

2701 Kent Avenue
West Lafayette
Indiana 47906

Table of Contents

Section 1. Introduction

The BAS RDE-2 Rotator is a miniature rotator system for use in constant-RPM and hydrodynamic modulation rotating disk electrochemistry. The short titanium shaft and 1/4" diameter electrode provide for an extremely low inertia system capable of highly accurate rotation and modulation, even at radical modulation rates or waveforms.

The rotator is electronically controlled by a proportional-integral closed loop circuit driving an ironless core DC servomotor. The rotator assembly is easily inverted for polymer spin coating directly on the unit. Electrodes are small and rapidly interchangeable. The unit also provides an adjustable valve system for inert gas purging and blanketing inside the cell vial.

The RDE-2 can be operated as a stand-alone unit or it can be controlled directly by BAS Electrochemical Analyzers or other voltage sources. It interfaces directly with BAS 100 series Electrochemical Analyzers as well as the CV-50W and other BAS Voltammographs. A built-in gas control allows purging or blanketing of the sample prior to or during analysis. The cell arm with detachable cell top allows easy access to the electrodes for rinsing, cleaning, or replacement. The cell vial base pivots for easy removal and replacement of the cell vial.

The RDE-2 is part of an Electrochemical Accessories Package. The package also includes voltammetry cells, reference electrodes (silver/silver chloride), a working electrode (glassy carbon), an electrode polishing kit, and connecting tubing.

Features

- Complete electrochemical accessories package:
  glassy carbon working electrode, three Ag/AgCl reference electrodes,
  reference electrode storage vial, platinum wire auxiliary electrode, polishing kit,
  vinyl gas line tubing, twelve standard cell vials, and cell top
- Remote or manual control of electrode rotation
- Small sample volume (10 - 15 mL)
- Water-jacketed cell vials available for purchase for controlled-temperature experiments
- “Quick-connect” input gas line connector
- Manual or remote control of purge/blanket lines
- Mounted cell top compatible with BAS reference and auxiliary electrodes
- Cell lead connects directly to all BAS potentiostats
- Standard addition port
- Open architecture for easy access to cell

Specifications and Technical Data

Size:	7.25" (18 cm) wide x 9" (23 cm) deep x 16.5" (42 cm) high
Weight:	12 lbs
Rotational Range:	50 to 10,000 RPM
Accuracy:	Error, < 2% at < 1000 RPM, < 1% at > 1000 RPM
Slew Rate (typical):	200,000 RPM/s (with shaft, brushes, and electrode)
Band Width:	60 Hz at 3500 RPM base and 1000 RPM peak-to-peak modulation
Rotator Shaft:	Titanium
Motor:	12 V, ironless core, low inertia DC servo
Motor Control:	Proportional-integral, closed feedback loop servo drive
Motor Protection:	Polymer PTC self-resetting overcurrent protection
Main Fuse:	4.0 A slow blow
Power:	< 100 VA, 100-240 VAC, 50/60 Hz
Operating Temperature:	10 to 50 °C (50 to 122 °F)
Inlet Gas Pressure:	5 psi maximum
Remote Control:	Speed control via external voltage source (1 V = 1000 RPM). Motor ON/OFF TTL or relay input to back panel connection. Purge/blanket TTL or relay input to back panel connection.

Accessories

Standard

Power Cord	ER-8502
Cell Vials (12)	MR-1208
Ag/AgCl Reference Electrode (3)	MF-2079
Platinum Wire Auxiliary Electrode	MW-1033
RDE-2 Operations Manual	MF-9006
Glassy Carbon Working Electrode	MF-2066
PK-4 Polishing Kit	MF-2060
BAS Cell Lead	EW-7524
BAS Remote Cable	EW-7526
Purge and Rotate Remote Cable	EW-7547

Optional

Platinum Working Electrode	MF-2067
Gold Working Electrode	MF-2068
Water-Jacketed Cell Vial	MR-1212

Standard electrode materials are glassy carbon, platinum, and gold. Electrode diameter is 3 mm. Electrodes of other materials and diameters will be fabricated on a custom basis. Call for a quotation.

BAS will also fabricate special purpose vials on a custom basis. Call for a quotation.

Section 2. General Information

User Updates

To receive product update news and valuable information related to this and other BAS products, fill out and return the BAS Warranty Enrollment Card shipped with your RDE-2. We would like to know who you are and how we can meet your electrochemical analysis needs.

Technical Changes

BAS may make technical changes to improve the instrument. Improvements affecting use or maintenance will be described in supplementary pages to this manual.

Shipping Damage

Damage to any part of the RDE-2 during shipping should be reported immediately to the freight handler and BAS Customer Service. Unless other arrangements have been made, the freight handler (shipper) is responsible for all damage or breakage to the instrument and parts. Retain the original packing box and contents for inspection by the freight handler. BAS will replace any new instrument damaged in shipping with an identical product as quickly as possible after the claim filing date. Claims not filed within seven (7) days after receipt of shipment may be invalid.

Do not return damaged goods to BAS without first contacting Customer Service for a Return Authorization Number (RA#). When a defective part is returned to BAS, the RA# immediately identifies you as the sender and describes the item being returned. BAS refuses all unauthorized return shipments.

Limited Warranty

BAS warrants equipment manufactured by the company to be free from defects in material and workmanship for a period of one year from the date of shipment, except as provided hereinafter. This warranty assumes normal usage under commonly accepted operating parameters. BAS agrees to either repair or replace, at its sole option and free of part charges to the Buyer, any parts of instrumentation which, under proper and normal conditions of use, prove to be defective within one year from the date of shipment. Electrochemical cells and working electrodes are warranted for 60 days. Expendable items including but not limited to carbon paste, reference electrodes, source lights, panel lights, fuses, etc., are excluded from the warranty. This warranty and remedy are given expressly and in lieu of all other warranties, expressed or implied, including but not limited to warranties of merchantability and fitness for particular purpose, and constitute the only warranty made by BAS.

BAS neither assumes nor authorizes any person to assume for it any other liability in connection with the sale, installation, service, or use of its instruments.

All products manufactured by BAS are tested and inspected prior to shipment. Upon prompt notification by the Buyer, BAS will correct any defects in warranted equipment of its manufacture either (at our option) by return of the item to our factory or shipment of a repaired or replacement part. BAS is not obliged, however, to replace or repair any piece of equipment which has been abused, improperly installed, altered, damaged, or repaired by others. Defects in equipment do not include decomposition, wear, or damage by chemical action or corrosion. Shipping charges under warranty are covered only in one direction. The Buyer is responsible for the cost of shipping to the factory if return of the part is required.

BAS shall have no liability whatsoever for special, consequential, or punitive damages of any kind arising from the sale, installation, use, or servicing of its instruments.

This instrument is manufactured for research purposes only. Use in medical diagnosis is not intended, implied, or recommended by the manufacturer. Use for this purpose and accountability for the same rest entirely with the user.

Service

BAS provides a skilled service staff to solve your equipment-oriented problems. For further details, call Customer Service at (765) 463-4527 or e-mail echem@bioanalytical.com. Following discussion of your specific difficulties, an appropriate course of action will be described and the problem resolved accordingly. Do not return any products for service until you have a return authorization number (RA#). Turn-around time on service can be estimated at the time your RA# is issued, but actual service required cannot be determined until we have received your unit and verified the problem. All correspondence and shipments should be sent to:

RA#________, Service Department
BAS
2701 Kent Avenue
West Lafayette, IN 47906

Section 3. Installation

Inspection of Shipment

After carefully unpacking the instrument, check the contents of the packages and inspect for damage. Parts of the RDE-2 are listed below. (This list is subject to change.) Please refer to the packing slip with your instrument to verify the parts. **Retain the shipping box and packing material until you have fully tested the unit to be certain that no damage was incurred during shipment.**

If you discover a shortage in parts, call BAS Customer Service and describe the shortage. Replacement part(s) will be sent immediately, subject to stock availability.

Parts of RDE-2

RDE-2

Glassy carbon electrode (1)

Voltammetry cell vials (12)

Teflon® cell top (1)

Polishing kit (1)

Ag/AgCl reference electrodes (3)

Platinum wire auxiliary electrode (1)

Standard addition port plug (1)

Gas connection tubing (1)

Cables

Instruction manual

Location of RDE-2

1. Provide a surge-free power source. Other laboratory equipment such as ovens, vortex mixers, centrifuges, and large motors may cause spikes in the power supply.

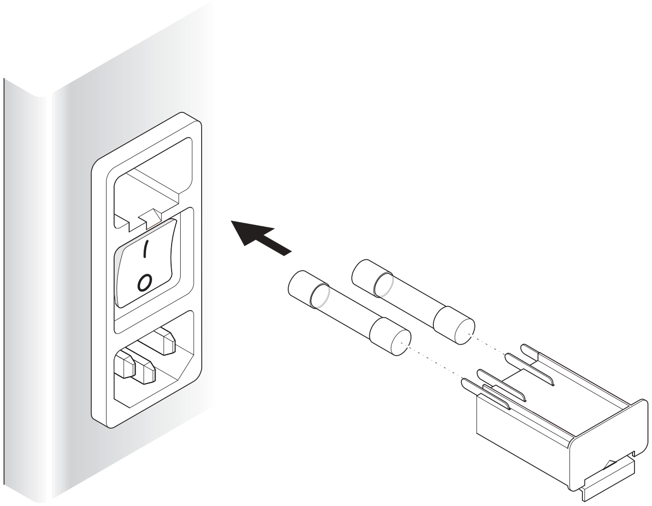
2. Ensure that all components of the system share the same ground circuit. This can best be accomplished by plugging all components into a multi-outlet power strip. Plugging the components into independent outlets can produce ground loops (current that flows between ground circuits at slightly different potentials), which can produce baseline noise.

3. Locate the RDE-2 on a stable bench. Vibrations can cause noise.
4. Select a room where temperature remains stable throughout the day. Avoid installing the RDE-2 near windows, air ducts, ovens, and refrigerators. Diffusion coefficients can change by 3%/°C. A water-jacketed cell may be required for very precise work.
5. Place the RDE-2 away from busy, congested areas. Remote, isolated areas are best for high-sensitivity work.
6. Avoid very dry areas and areas that are carpeted. Static electricity can affect instrument performance. Anti-static floormats and benchmats are useful if spiking caused by static charge is a problem.
7. Avoid areas where radio-frequency interference is likely. Beeper-type paging devices can be a problem in some installations.

Power Requirements

The RDE-2 contains a fused, self-sensing power supply which can be powered by 100-240 V (50-60 Hz) (see Figure 1). It uses two 4 Amp fuses. Power requirements are shown on the back panel of the RDE-2 (see Figure 2).

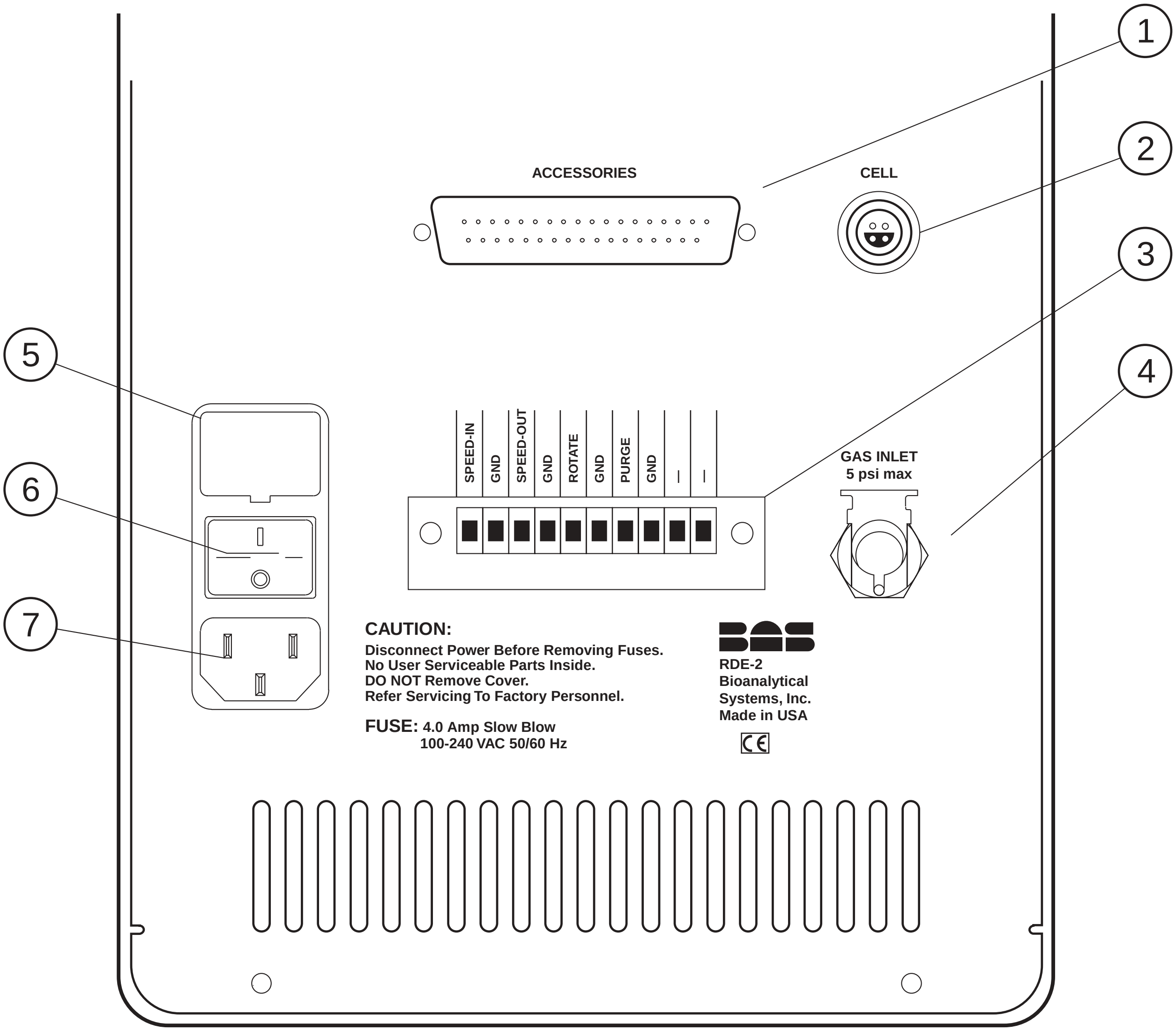
Figure 1. Fuse Placement



Back Panel Controls and Connections

1. Remote Connector. 37-pin ribbon cable used with BAS 100 B/W
2. Cell Lead Connector.
3. Screw Terminal
4. Gas Inlet Connector for Cell Purging. Bulkhead fitting providing connection to external gas source. **NOTE: 5 psi maximum.**
5. Fuse Holder.
6. Power On/Off Switch.
7. Power Cord. Be sure that the 3-prong power cord is connected to a grounded circuit.

Figure 2. Back Panel



Making Connections

Power Cord Connection

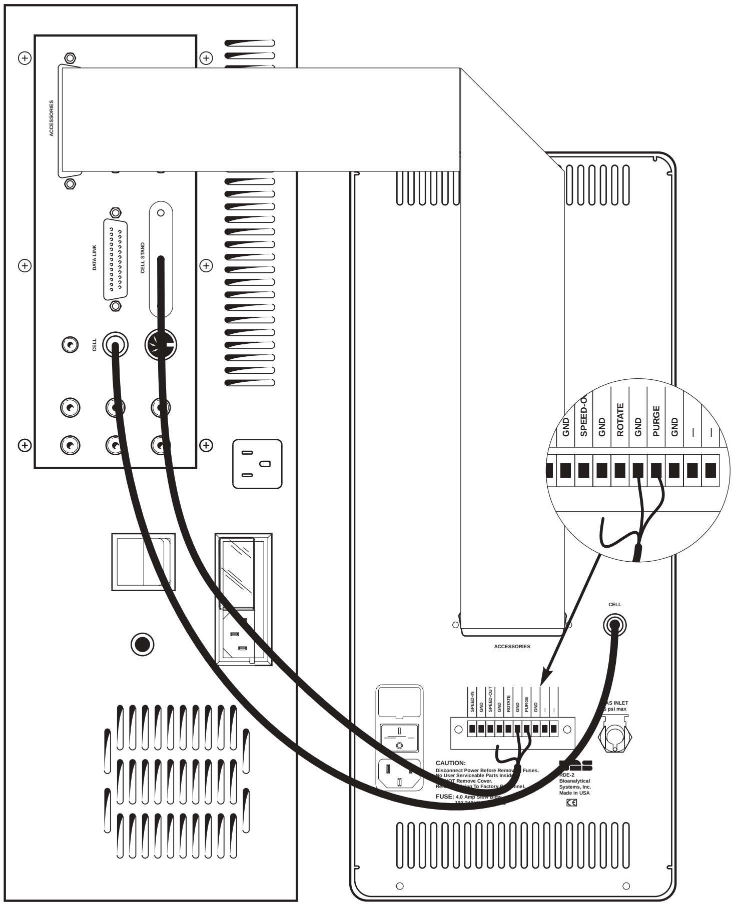
Push the socketed (female) end of the power cord into the port located in the back panel. Before making this connection, make certain that the power on/off switch is in the off position. This switch is labeled with a 0 and a 1. When 0 is pushed, the power is off and when 1 is pushed, the power is on.

RDE-2 to BAS 100A/B Series Electrochemical Analyzer

Three cables are required to connect the RDE-2 to the BAS 100A/B series. Electrode rotation can be automatically controlled by the BAS 100A/B series. The control cable is a 37-line ribbon cable (EW-7526) between the ACCESSORIES connector (37-pin D, male) on the back of the RDE-2 and the ACCESSORIES connector (37-pin D, female) on the back of the BAS 100A/B series. See Figure 3.

In order to control purging remotely, the purge and rotate remote cable (the one with three stripped wire ends) should be connected to the screw terminal on the back of the RDE-2. Follow the labels on the wire ends and the screw terminal. Since the 37-pin cable controls the electrode rotation, the rotation lead <u>should not be connected</u>. The other end of this cable should be connected to the CELL STAND port on the back of the potentiostat. See Figure 3.

Figure 3. Connection of RDE-2 to BAS 100 Electrochemical Workstation



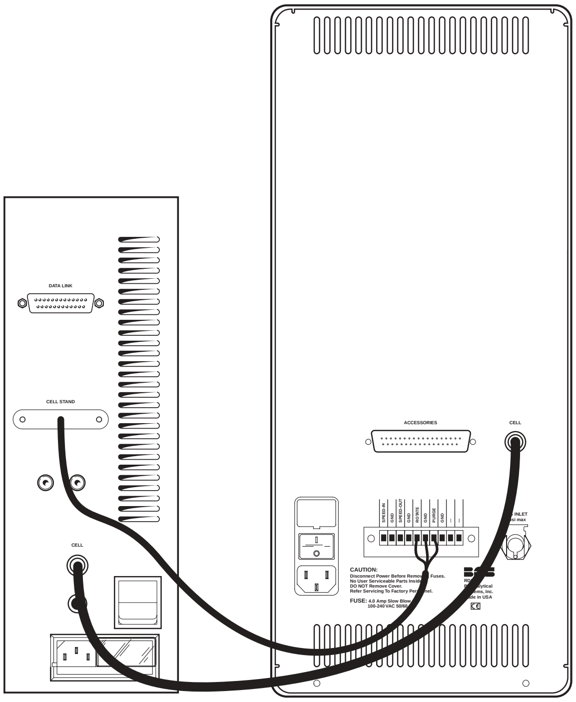
Connection of the cell lead cable is also shown in Figure 3. The cell lead cable has a stainless steel LEMO connector at each end. One end is inserted into the CELL socket on the back of the RDE-2. The other end is inserted into the CELL socket in the back of the BAS 100A/B series. The ends are identical; therefore, it does not matter which end is connected to the BAS 100A/B series or the RDE-2.

RDE-2 to CV-50W Voltammetric Analyzer

Two cables are required to connect the RDE-2 to the CV-50W. In order to control rotation speed and purging remotely, the purge and rotate remote cable (the one with three stripped wire ends) should be connected to the screw terminal on the back of the RDE-2. Follow the labels on the wire ends and the screw terminal. The other end of this cable should be connected to the CELL STAND port on the back of the potentiostat. See Figure 4.

Connection of the cell lead cable is also shown in Figure 4. The cell lead cable has a stainless steel LEMO connector at each end. One end is inserted into the CELL socket on the back of the RDE-2. The other end is inserted into the CELL socket on the back of the CV-50W. The ends are identical; therefore, it does not matter which end is connected to the CV-50W or the RDE-2.

Figure 4. Connection of RDE-2 to CV-50W Voltammetric Analyzer



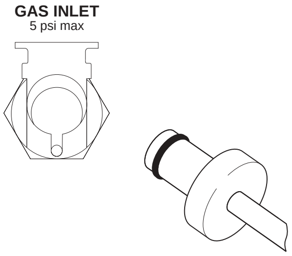
RDE-2 to Non-BAS Instruments

The RDE-2 should work, at least in the manual mode, with virtually any instrument. Cables must be custom made by the user. The CELL cable is modified by cutting off one of the LEMO connectors and attaching the appropriate connector for the particular instrument. The color code for internal wires is red (auxiliary electrode lead), white (reference electrode lead), black (working electrode lead), and bare (ground).

Gas Inlet Connection

The RDE-2 package contains 0.25" OD tygon tubing and a gas line fitting. One end of the gas line fitting is barbed to fit inside the tygon tubing. Push the barbed end into the tubing. The other end of the fitting connects to the GAS INLET port on the rear panel of the RDE-2 (Figure 5). To attach the line, simply push the connector into the port. A retaining clip will snap into place. The open end of the tygon tube is connected to a regulated gas supply. Inlet gas pressure must not exceed 5 psi. To remove the tube from the RDE-2, squeeze the retaining ring tab against the connector, then pull tube and connector away from the RDE-2.

Figure 5. Gas Line Connection to RDE-2



Cell Placement

The RDE-2 is designed for easy cell replacement and to accommodate both regular cells and water-jacketed cells. The cell is held in place by the cell base and the cell top. Follow these instructions for initial cell placement:

1. Pivot the cell base to the right.
2. Bring the cell up from underneath, around the electrodes, and seat on the cell top.
3. Pivot the cell base back under the cell.
4. If required, the cell top height can be adjusted by loosening the cell top height adjustment knob, sliding the cell top assembly to the desired position, and tightening the knob.
5. Three 0.25" holes are in the cell top. These holes are for the reference electrode, auxiliary electrode, and standard addition. Place the electrodes and port plug in the holes which are the most convenient.

Purge/Blanketing Lines

The RDE-2 has the ability to purge or blanket the sample solution with an inert gas. The purge removes oxygen by bubbling with an inert gas, typically nitrogen or argon, through the solution. The blanketing function is to maintain an inert atmosphere above the sample to keep oxygen from re-entering the sample solution.

The purge/blanket lines are the two plastic (Teflon) tubes coming out of the cell top support block. These two lines should be pressed into the Teflon cell top. The blanket line should extend to just beyond the bottom of the cell top. The depth of the purge tube should be near the bottom of the cell vial.

In order to access the purge tubing when the RDE-2 is lowered, pull out extra length of the tubing and curve it around the side of the electrode.

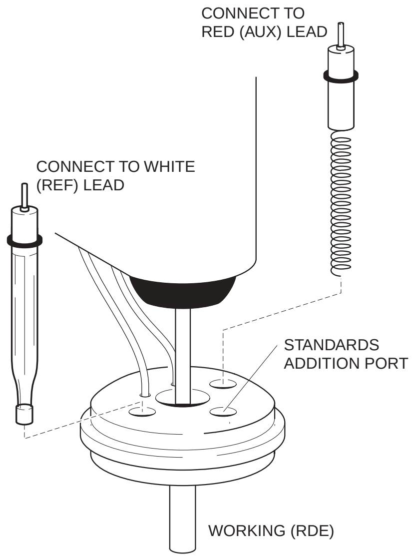
Electrode Leads

The reference and auxiliary electrode lead wires extend through the front panel. The connectors are the spring-loaded, press-on type. Simply push the connector over the corresponding pin in the electrode to make the connection (Figure 7). Each wire is color coded to the electrode it attaches. The code is:

White . . . . Reference Electrode
Red . . . . Auxiliary Electrode

Alligator clips with the appropriate pin and colored boot are included for connection to electrodes that cannot be connected to the sockets on the cell lead.

Figure 6. Electrode Lead Connections

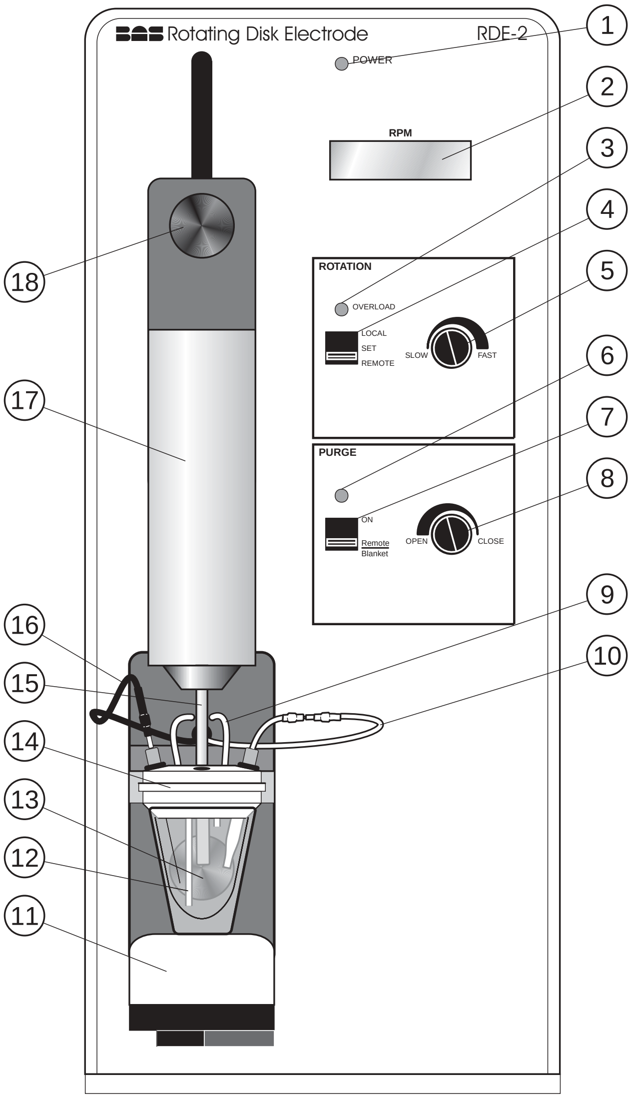


Front Panel Controls and Connections

1. Power LED. LED is lit when RDE-2 is powered (on/off switch is located on back panel).
2. Digital RPM Display.
3. Overload LED.
4. Rotation Control Switch. Allows toggling between REMOTE and LOCAL operation via SET position. In manual or remote operation with BAS CV-50W Electrochemical Analyzer, the RPM is set in the SET position.

5. Rotation Rate Setting Knob.
6. Gas Purge LED. LED is lit when gas purge is turned on for sample vial, either manually or remotely. When LED is off the gas flows through the blanket line.
7. Gas Purge Control Switch. When switched to REMOTE/BLANKET, the gas flows through the blanket line. For manual purging, switch to ON position.
8. Gas Purge Flow Control. Needle valve control of gas flow to purge and blanket lines.
9. Gas Blanket Line.
10. Reference Electrode Lead. White lead connected to reference electrode.
11. Cell Base.
12. Gas Purge Line.
13. Cell Top Height Adjustment Knob.
14. Teflon Cell Top.
15. Rotator Shaft.
16. Auxiliary Electrode Lead. Red lead connected to platinum wire auxiliary electrode.
17. Rotator Motor Housing.
18. Electrode Height Adjustment Knob.

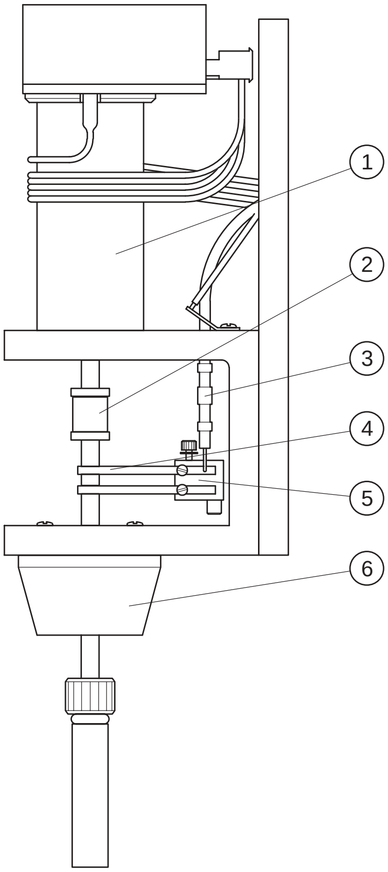
Figure 7. Front Panel



Section 4. Motor and Working Electrode Assembly

1. Rotator Motor. 12V ironless core servomotor with integral digital tachometer. Wires from the motor and elsewhere pass through a strain-relief ziptie.
2. Shaft Coupler. Insulating sleeve clamped by two dynamically balanced hub clamps.
3. Brush Connector. Disconnects for easy replacement of the brush assembly. Also transfers the working signal to shielded cable.
4. Brushes.
5. Brush Block Assembly. Four silver-graphite leaf-spring brushes mounted directly on a small insulator block. All four brushes connected in parallel before entering the brush connector.
6. Bearing Housing. Precision ball bearing in an insulator housing.

Figure 8. Motor and Working Electrode Assembly



Section 5. Operation

Remote Control

The remote connectors of the RDE-2 allows rotation and gas purge functions to be controlled by an external unit. The RDE-2 was specifically designed to be controlled by the appropriate commands from the BAS 100A/B Series Electrochemical Analyzer and CV-50W. These functions can be activated by either a TTL signal or from any controller providing a contact closure to the ground. All lines are active low (negative edge triggered).

Follow operational instructions given under “Initial Instrument Operation” for remote rotation.

Gas Purge

The flow rate of the gas and whether it is directed to the purge or blanket lines is controlled by a front panel knob and switch. When toggled to the ON position, the gas flow is directed to the purge line and cannot be changed by remote control. When switched to the REMOTE/BLANKET position, the gas is directed to the blanket line. It must be in this position to externally control PURGE via the REMOTE connector on the back panel. The LED is lit when the purge function is on, either manually or remotely.

To control purge remotely, the purge and rotate remote cable should be connected on the back panel of the RDE-2. Time of purging can be controlled manually or via the “immediate purge/rotate” option under the control menu of the BAS operating software.

General Instructions

The power switch on the back panel should be in the OFF position. The Rotator is then connected to the mains with the power cable included with delivery. The mains connection must have proper grounding.

WARNING: Any disconnection of the ground wire either inside or outside the instrument may be dangerous. DO NOT DISCONNECT!

Turn on power and raise the chassis to the top of the unit by loosening the height adjustment knob. Set the LOCAL/SET/REMOTE switch to LOCAL and turn the RPM Adjust knob clockwise until the display reads approx. 500 RPM. Visually inspect the shaft and electrode body for any obvious wobble during rotation. Check that the top of the electrode body rests lightly against the white O-ring on the shaft. Stop rotation by switching to SET.

The solution should be thoroughly purged before use with the gas purging function on the front panel of the unit. The most effective purging is done by using a low-pressure inert gas source connected to the gas fitting on the rear panel. The GAS ADJUST valve on the front panel controls the rate of purging.

Initial Instrument Operation

With all front and back panel connections made, follow the procedure below for the initial use. (Requires connection to BAS CV-50W or 100B/W Electrochemical Analyzer.)

1. Place the LOCAL/SET/REMOTE, 3-position switch (Figure 7, item 4) in the SET, middle position.

2. Push the rear panel power switch to the on (“1") position.

3. Loosen the height adjustment knob and slide the electrode holder as far up as it will go. Tighten the knob.

4. Remove the electrode by holding the shaft skirt and turning the electrode body counterclockwise (Figure 10). Polish the electrode by following the instructions in the Polishing Kit. See Section 6 for more information.

5. Replace the electrode (see Section 6). Note that a slight upward pressure must be applied to the electrode body to start the threads.

6. Place a test solution in the cell vial. A common test solution is 2 mM potassium ferricyanide in 1 M KCl.

7. With the cell vial in place, lower the rotator assembly onto the cell vial by loosening the height adjustment knob.

8. Place the reference and auxiliary electrodes in two of the holes in the cell top and attach the cell leads. Start purging the solution with inert gas as described previously. For this initial experiment, purging 5-10 minutes will be adequate.

9. In Setup under the FILE menu, set SMDE as the CELL STAND.

10. If the RDE is being used with the BAS 100B/W, push the LOCAL/SET/REMOTE switch to the Remote position and fix the rotation rate to 400 RPM using the RDE Technique and entering 400 as the rotation rate in the General Parameter window. If prior rotation is necessary for mixing purposes, it can be achieved manually from the front panel or remotely via IMMEDIATE PURGE/STIR option under the CONTROL menu.

11. If BAS CV-50W is being used, set the rotation rate to 400 RPM manually at the SET position and switch to LOCAL position. Now the 50W software will turn rotation on and off remotely.

12. The instrument is ready for use. The electrode will begin to spin when the RUN command is initiated in the software.

Typical test parameters are:

Working Electrode:	3 mm glassy carbon
Reference Electrode:	Ag/AgCl
Auxiliary Electrode:	Platinum Wire
Test Solution:	2 mM Ferricyanide/1M KCl
Initial E:	+600 mV
Final E:	+100 mV
Scan Rate (V):	20 mV/S
Rotation Rate:	400 RPM
Sensitivity:	10E-5 (10s of microamperes)

13. After the experimental run, the Rotator Housing can be raised and the electrodes can be rinsed or polished as needed. The system is then ready for the next experiment.

Spin Coating

To perform coating, raise the electrode assembly as far as it goes by loosening the electrode height adjustment knob. Secure the electrode at this position by tightening the height adjustment knob. Now turn the rotator motor housing (Figure 7) 180° counterclockwise to an exact vertical position with the electrode facing straight up. While at this position, if necessary, the electrode can be lowered and secured again.

A spin coat adapter has been provided with the instrument for convenient spin coating of working electrode surfaces. When placed over the electrode (Figure 9), it prevents splashing of the coating material on to the RDE-2, its surrounding, and the operator. Apply the appropriate amount of coating material on the electrode surface and place the plastic spin coat adapter over the electrode as shown in Figure 9. Care should be taken not to overload the electrode with the coating material. Any spillage should be cleaned immediately as some organic material could be harmful to the finished surfaces of the RDE. Rotate the electrode at a predetermined RPM to achieve your desired coating.

Once finished coating the electrode, remove the adapter and clean the splashes. Remove any spillage on the rotator assembly and the surrounding surfaces as well. Do not use alcohol or acetone to wash the adapter as organics may cause it to crack. Soap and water should be adequate for this purpose. Dry the adapter and store in a safe place. Cure the coating.

If the electrode was lowered from its highest position before the coating procedure, raise it again and secure. Turn the assembly by 180° clockwise to a vertical position with the electrode facing straight down. Lower the electrode through the center hole of the cell top into the cell vial containing the analytical sample. Use it in the usual manner after completing the three-electrode system.

Figure 9. Rotation of Electrode for Spin Coating Surface

Section 6. Maintenance

General Maintenance

The RDE-2 is a very rugged instrument and, with proper care, should give years of service. Following is a brief list of cautions and general maintenance considerations that will extend the lifetime of the instrument.

- Follow customary, good laboratory practices.
- Clean all spills, especially salt solutions, on or near the cabinet immediately.
- Avoid placing the unit in a corrosive atmosphere.
- Avoid dropping, shaking, or other forms of mechanical abuse to prevent loosening of components or subassemblies.
- Clean gas lines (rinse and wipe dry) after each use.
- Do not bend the auxiliary electrode (platinum wire) when removing or placing the cell vial. Repeated bending will cause the wire to break.

Changing the Working Electrode

Attach the electrode body to the protruding shaft by threading it on lightly, while holding the shaft steady with the knurled shaft skirt. DO NOT BEND! Be careful and turn slowly — you should feel the contact plunger compress against the electrode material. Turn the electrode until it rests lightly against the teflon (TFE) O-ring. DO NOT OVERTIGHTEN! If the electrode is overtightened, it will align with the very end of the threaded portion of the shaft and will be eccentric. By threading the electrode against the O-ring, the ground diameter of the shaft will align the electrode and allow for a more consistent position.

To remove, reverse above operations.

Figure 10. Working Electrode Assembly

Repolishing Electrodes

1. Carefully remove the electrode as outlined above.
2. Polish the electrode according to instructions enclosed in the PK-4 Polishing Kit that comes with the RDE accessories.

The objective of polishing the electrode is to remove the products of the redox reaction or physical adsorption which accumulate during some experiments. The rate of electrode coating (and corresponding decrease in responsiveness) will depend upon the following factors:

a. Analyte molecule
b. Concentration of the analyte molecule
c. Composition of stationary phase
d. Applied potential
e. Frequency of use

Electrodes used in electrochemistry could need repolishing after each experiment, depending on the application. Rotating disc and hydrodynamic modulation applications have the advantage of a moving solution which helps to remove redox products and often deals with lower concentrations of analyte than are typically seen with voltammetry methods in nonstirred solutions. The need for polishing varies greatly with the application. The general rule is that polishing is justified when a gradual decrease in electrode response is observed. Electrodes also can accumulate contaminants by adsorption from the environment. Cigarette smoke, aerosols, and other airborne materials can be adsorbed quite easily.

The polishing process should remove a negligible amount of electrode material. A series of one to three different abrasive systems are used, progressing from coarse particle sizes to very fine polishing powders. Most electrode surfaces need only a single polishing step to physically remove the contaminants. Precious metal (gold, silver, and platinum) electrodes may do best with either an alumina or a diamond polish. It is best to start with the diamond polish and then determine if the desired results are obtained with that step alone. Chemically modified (gold/mercury amalgam) and glassy carbon electrodes tend to require a two or three step series of abrasives to restore the original mirror-like finish.

All polishing steps require extensive rinsing and flushing of the electrode before moving on to the next stage. Without thorough washing, minute particulate from the previous polishing step will hinder the progression towards a finely polished surface. A major concern of polishing is that you do not erode the softer electrode material below the the level of the supporting plastic or glass. This can be avoided by always polishing the electrode on a very flat surface. Always follow the general precautions listed below when handling your working electrode:

a. It is important that you use only BAS-manufactured polishing materials and that you follow the recommended procedure. The PK-4 kit provides the materials needed for all polishing procedures.

b. Polish the electrode on pads attached to the heavy glass provided in the polishing kit. You must keep the electrode surface as parallel to the surface of the glass as possible when polishing. This is especially important with the RDE Working Electrodes and will ensure that the surrounding plastic is not worn unevenly. You must be sure to polish very slowly to maintain the surface as flat as possible. Any deviation will be obvious when the electrode rotates.

c. Never attempt to remove the actual electrode material from the supporting plastic. This will destroy the electrode.

d. Do not heat the electrodes when drying; allow them to dry at room temperature. Heating will cause problems due to the difference in the coefficients of expansion of the electrode material and the supporting plastic or glass.

e. You must be very careful that no debris enters the open back of the electrode body. The opening must be kept clean in order for the spring-loaded plunger to effectively contact the electrode material.

3. Carefully replace the electrode on the rotator as described in the previous section.

Replacing Rotator Shaft

1. Carefully insert the shaft assembly through the bearing housing and into the ball bearing. The shaft should ride smoothly in the bearing with a good sliding fit. Using a small probe, move the brushes out of the way one at a time and slide the shaft into the coupler. Be careful that the two align and fit smoothly. Spin the motor and observe the end of the shaft. It should turn in a tight, concentric circle around its axis.

2. Tighten the coupler clamps (motor side clamp first) until the shaft and motor are firmly gripped by the coupler. You should alternately tighten each screw a small amount so that the gaps on each side of the clamp remain even during the entire process.

3. Replace the chassis cover.

4. To remove, reverse above operations.

Replacing Rotator Bearing

Gently slide the bearing housing into the opening in the bottom of the rotator chassis. Bolt the housing into place with three #4-40 socket-head cap screws. Alternately tighten each screw a small amount at a time so that the housing is seated evenly. See Figure 8.

Replacing Working Brushes

1. Remove rotator shaft (see Figure 8).

2. Remove old brush block.

3. Place the new brush block inside the chassis so that the dowel pin in the block is in the small hole in the chassis. Secure with a #4-40 x ½ socket-head cap screw. Make sure that the brushes are centered over the bore in the bearing housing.

4. Connect the brush block assembly to the 1/8" diameter shielded cable.

5. Replace the shaft assembly. Be careful as you move the brushes to insert the shaft assembly.

6. Make sure the brushes are evenly spaced and perpendicular to the rotator shaft.

Replacement Parts

Brush Block Assembly	MW-2450
Bearing Housing Assembly	MW-2400
Shaft Assembly	MW-2130
Shaft O-ring	MR-1241

Troubleshooting

Symptom	**Cause**	**Solution**
saturated signal	reference tip not in contact with solution	lower reference
noisy signal	clogged reference frit	replace reference
	air bubble in reference tip	“flick” reference until bubbles are at top
	vibrations	place on pad to dampen vibration
	spikes in power line	power from a different circuit
variation in peak height	temperature variation	use water-jacketed cell

Service Procedure

All other service should be referred to BAS service personnel. In certain cases, BAS will provide electronic schematics and service procedures to qualified electronic maintenance facilities, but only upon written request and then only with the approval of the Service Coordinator. If a problem arises and appears equipment oriented, call BAS at (765) 463-4527 and ask for Customer Service, or e-mail echem@bioanalytical.com.

Appendix I. Rotating Disk Voltammetry

The basis of voltammetry is the measurement of the current response to an applied interfacial potential. The magnitude of this current can be affected by both the rate of charge transfer between the working electrode and the interfacial solution, and by the rate of mass transport from the bulk solution to the electrode surface. The first of these variables is controlled by the applied potential, but the nature of the mass transport depends on the experiment.

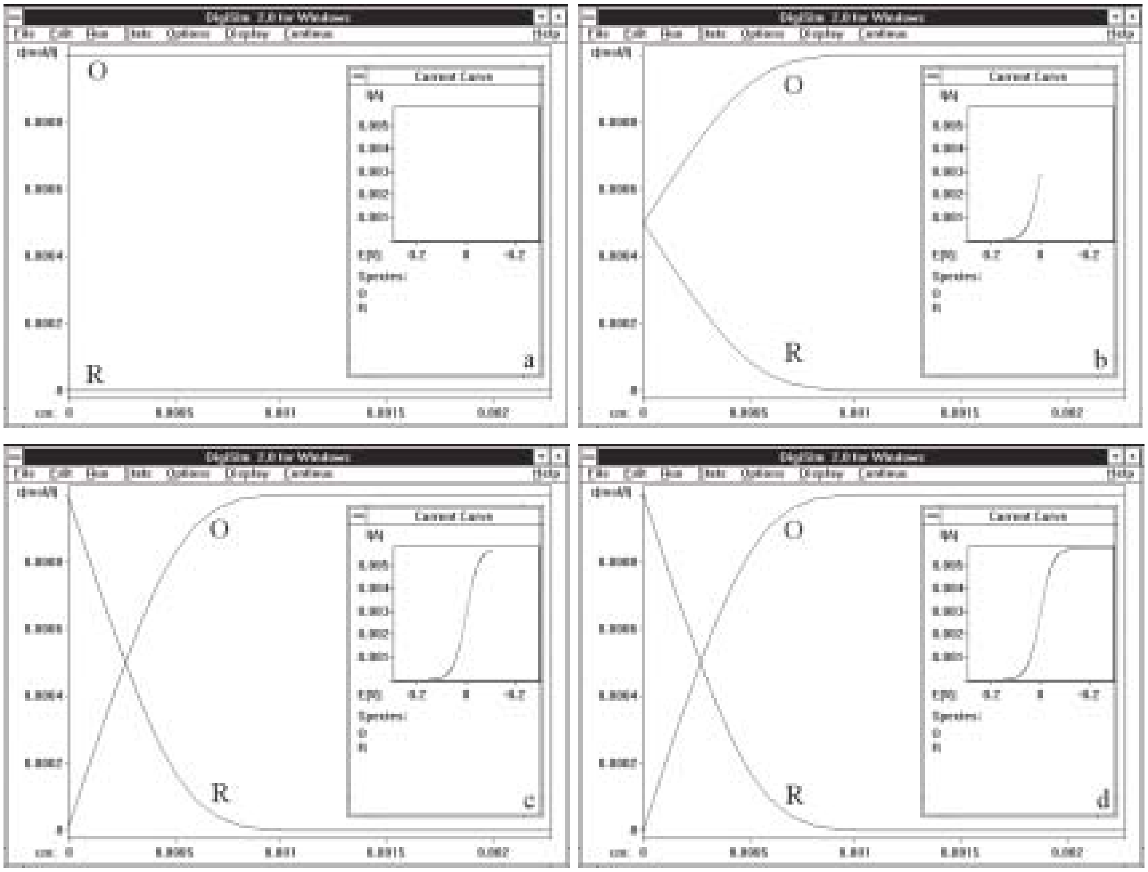
There are three types of mass transport:

- Diffusion — molecular motion down a concentration gradient
- Convection — molecular motion imposed by external influences (vibrations or stirring)
- Migration — molecular motion down an electric gradient

To extract quantitative data from electrochemical experiments, the mode of mass transport must be experimentally controlled, and must be stable for the duration of the experiment. Migration of the electroactive molecules is eliminated by using the supporting electrolyte to carry the current. Convection can also be eliminated by using an unstirred solution. These conditions are used for many voltammetric experiments (e.g., cyclic voltammetry, chronocoulometry, and pulse techniques), where diffusion is the only form of mass transport available. Although this process is mathematically well defined, diffusion-only conditions cannot be maintained for a extended period of time, since it is difficult to completely eliminate natural convection (e.g., due to vibrations and density gradients). In addition, there is no way to control the rate of diffusion (although varying the temperature does change the rate of diffusion, it also affects the rate of electron transfer and chemical reactions and it is difficult to separate the different effects).

There is a group of electrochemical experiments (called hydrodynamic techniques) in which forced convection of the solution is used (1,2). The mass transport in these experiments is a combination of convection and diffusion. The solution can be divided into two areas, the bulk solution (convection) and the diffusion layer (diffusion). In the bulk solution, there is mass transport by convection. At large distances from the working electrode, the solution flow is turbulent. However, this turbulence decreases nearer the electrode and there is a transition to laminar flow, in which the solution layers slide past each other parallel to the electrode. The rate of this flow decreases nearer the electrode due to frictional forces, and the layer immediately adjacent to the surface of the electrode is stationary. This layer is called the diffusion layer, and is often represented by the symbol d. Therefore, the electroactive molecules are moved from the bulk solution to the edge of the diffusion layer by convection, and motion across this layer occurs by diffusion down a concentration gradient. The rate of this mode of mass transport is faster than can be achieved by diffusion alone, and, unlike diffusion, it is independent of time. The other advantages of convection-diffusion are that the mass transport is stable and often mathematically well defined, and it can be controlled by varying the rate of stirring. For example, increasing the rate of stirring increases the rate of convection to the edge of the diffusion layer, and the thickness of this layer is decreased. Therefore, there is a greater degree of control of the experimental parameters than there is in cyclic voltammetry and other non-hydrodynamic experiments.

F1. Concentration profiles for the redox reaction O + e = R at a rotating disk electrode. These plots were generated from BAS Digisim® simulation software.



The current response in a hydrodynamic experiment has a characteristic sigmoidal shape (**F1**), and the reason for this can be explained using the Nernst equation and the concentration profiles shown in **F1**. For a solution containing only O at a potential well positive of the formal reduction potential, the Nernst equation requires that the surface concentration of R (C^S_R) is zero (**F1a**). However, as the reduction potential is approached, net conversion of O to R at the electrode surface is required (at $E^{O'}$, the equilibrium values of C^S_O and C^S_R (i.e., the values required by the Nernst equation) must be equal (**F1b**). Thus, there is a net cathodic current, which has an exponential dependence on the applied potential. However, this exponential dependence is modified by the depletion of the concentration of O at the electrode surface, and the rate of mass transport from the bulk solution must also be considered. In cyclic voltammetry, the only mode of mass transport is diffusion from the bulk solution. This process depends on $t^{-1/2}$, so the mass transport limited current (limiting current) in cyclic voltammetry depends on $t^{-1/2}$. In hydrodynamic voltammetry, the diffusion layer is typically smaller than it is for cyclic voltammetry and is independent of time (**F1b-d**), so O is brought to the electrode (and R is removed) at a much faster rate that is independent of time. Therefore, rather than decaying, the limiting current is a plateau (**F1d**), the magnitude of which is determined by the thickness of the diffusion layers. The limiting current i_l for a reversible (fast) process is given by the equation

$$i_l = nFADC/\delta$$

where D is the diffusion coefficient (cm^2 s^{-1}). The potential at $i_l/2$ ($E_{1/2}$) is a good approximation to the formal redox potential ($E^{0'}$) provided the diffusion coefficients for O and R are similar.

The fast time-independent mass transport also means that, at a given potential, a steady-state is rapidly achieved (i.e., the rates of mass transport and charge transfer are balanced). Steady state conditions can be maintained during a potential scan if the scan rate is sufficiently slow (about 20 mV/sec). Under these conditions, the current at a given potential is independent of both the scan direction and time. Another advantage of steady-state conditions is the relative freedom from charging currents.

Although forced convection can be achieved using a stationary electrode in a stirred solution, it is more common to use a rotating electrode. The electrode can be a disk, a ring or a combination of the two. The range of rotation rates (angular velocities) is generally between 100 and 10,000 rpm (10 and 1000 radians s^{-1}). For a rotating disk electrode (RDE) δ is given by the equation:

$$\delta = 1.61D^{1/3}\upsilon^{1/6}\omega^{-1/2}$$

where ω is the angular velocity of the electrode and υ is the solution viscosity (cm^2 s^{-1}).

Therefore, i_l for a reversible process for an RDE is

$$i_l = 0.62nFACD^{2/3}\upsilon^{-1/6}\omega^{1/2}$$

In summary, the principal advantage of rotating disk voltammetry is that steady state, rather than transient, conditions apply. The relative freedom from double-layer charging effects and the steady-state background current are key advantages of steady-state techniques that cyclic voltammetry does not have. It can be used to measure rates of reactions at the electrode surface (including rates of electron transfer and substrate diffusion through adsorbed polymer films) and in solution. The precise control of stirring that is possible with a rotating disk electrode makes this electrode ideal for quantitative analysis studies based on stripping voltammetry. The success of liquid chromatography with electrochemical detection (LCEC) is based on the same principle. The low detection limits of LCEC are a direct result of the steady-state background and the freedom from double-layer charging currents. Hydrodynamic techniques often exhibit detection limits two or three orders of magnitude better than other electrochemical techniques.

References

1) P.T. Kissinger and W.R. Heineman (eds.), Laboratory Techniques in Electroanalytical Chemistry, Dekker, New York, 1984, Chap. 3.

2) A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980, Chap. 8.

3) A.W. Bott, Current Separations 12:1 (1993) 21.