

Model 366A

BI-POTENTIOSTAT

Hardware User's Manual

Advanced Measurement Technology, Inc.
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6. Symptoms (in detail, including control settings).
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TABLE OF CONTENTS

Safety Instructions and Symbols	iv
Cleaning Instructions	iv
1. GENERAL	1
1.1. INTRODUCTION	1
1.3. INITIAL INSPECTION	2
1.4. SAFETY CONSIDERATIONS	2
1.5. POWER VOLTAGE SELECTION	3
1.6. LINE FUSE REPLACEMENT	4
1.7. SERVICE	4
1.8. GENERAL DESCRIPTION	5
1.8.1. Sweep Generator	5
1.8.2. Potentiostat	5
1.8.3. Galvanostat	6
1.8.4. Voltmeter	6
1.9. SPECIFICATIONS	6
1.10. SWITCH AND POTENTIOMETER FUNCTIONS	7
1.10.1. Sweep Generator Section	7
1.10.2. K1 and K2 Electrode Section	8
1.11. JACK FUNCTIONS	8
Front Panel	8
Rear Panel	9
1.12. NOISE AND OSCILLATIONS	9
1.13. CIRCUIT DESCRIPTION	10
2. THEORY	13
2.1. THE DIFFUSION LAYER	13
2.2. THE ROTATING DISK ELECTRODE	14
2.3. THE ROTATING RING-DISK ELECTRODE (RRDE)	18
2.4. SURFACE CONTROLLED ELECTRODE CURRENT	20
2.5. DIFFUSION LAYER TITRATIONS	23
2.6. LITERATURE CITED AND FURTHER READING	24
3. ELEMENTARY EXPERIMENTS	25
3.1. EQUIPMENT AND SOLUTIONS	25
3.2. EXPERIMENT A: RESIDUAL CURRENT-POTENTIAL CURVE FOR Pt ELECTRODES IN ACIDIC SOLUTIONS	26
3.3. EXPERIMENT B: MASS TRANSPORT-LIMITED CURRENTS AT THE ROTATING DISK ELECTRODE	29
3.4. EXPERIMENT C: COLLECTION AND SHIELDING EFFICIENCY OF A ROTATING RING-DISK ELECTRODE	32
4. PRELIMINARY TESTING	37
4.1. INTRODUCTION	37
4.2. TROUBLESHOOTING	38
INDEX	41

Safety Instructions and Symbols

This manual contains up to three levels of safety instructions that must be observed in order to avoid personal injury and/or damage to equipment or other property. These are:

DANGER Indicates a hazard that could result in death or serious bodily harm if the safety instruction is not observed.

WARNING Indicates a hazard that could result in bodily harm if the safety instruction is not observed.

CAUTION Indicates a hazard that could result in property damage if the safety instruction is not observed.

Please read all safety instructions carefully and make sure you understand them fully before attempting to use this product.

Cleaning Instructions

WARNING Using this instrument in a manner not specified by the manufacturer may impair the protection provided by the instrument.

To clean the instrument exterior:

- Unplug the instrument from all voltage sources.
- Remove loose dust on the outside of the instrument with a lint-free cloth.
- Remove remaining dirt with a lint-free cloth dampened in a general-purpose detergent and water solution. Do not use abrasive cleaners.

CAUTION To prevent moisture inside of the instrument during external cleaning, use only enough liquid to dampen the cloth or applicator.

- Allow the instrument to dry before reconnecting the power cord.

1. GENERAL

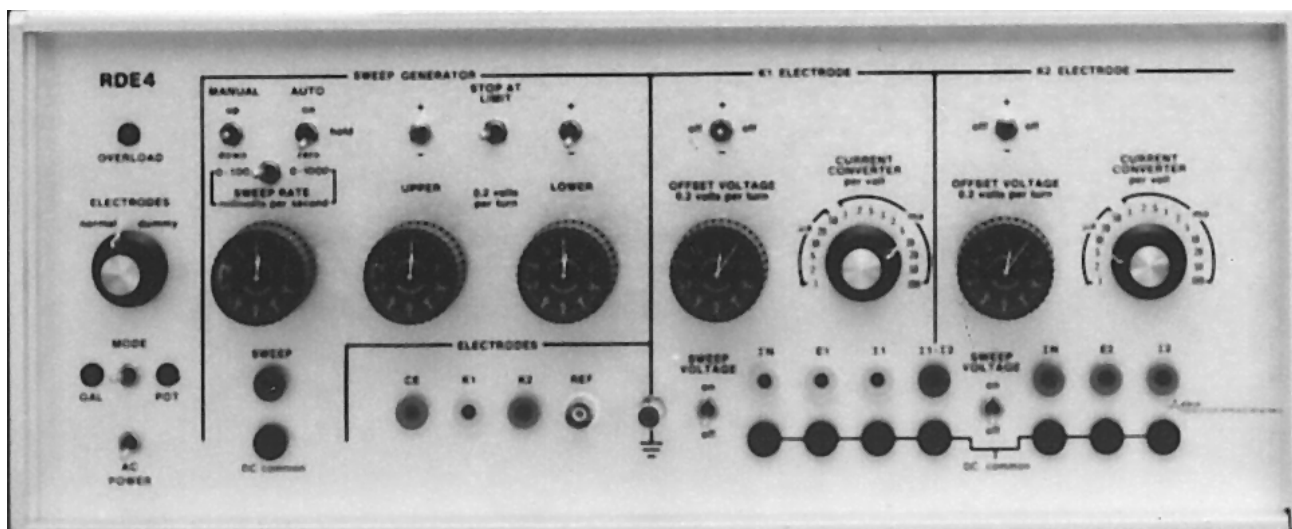


Fig. 1. MODEL 366A BI-POTENTIOSTAT.

1.1. INTRODUCTION

The Princeton Applied Research Model 366A Bi-Potentiostat is a four-electrode potentiostat designed to be used with a ring-disk electrode. It can control two working electrodes at different potentials and monitor the currents generated at these electrodes. Although it has been engineered specifically for ring-disk electrodes, it can also be used with nonrotating electrodes and a variety of cell configurations.

The Model 366A can be used in potentiostat mode for both working electrodes, or one of the electrodes can be controlled galvanostatically while the other is controlled potentiostatically. The Model 366A includes a built-in sweep generator which is set by specifying sweep rate rather than frequency or period. The potential of one or both electrodes may be swept. Additionally, an externally generated waveform may be applied to the electrodes. The bi-potentiostat can also be used in the conventional three-electrode arrangement.

The bi-potentiostat is particularly useful to researchers interested in reaction kinetics and reaction mechanisms. In one use the disk of a rotating ring-disk electrode can be cycled between potentials while the ring is held at constant potential. If the appropriate choices are made for these values, materials formed at the disk can be detected at the ring. This allows the researcher to detect reaction intermediates and, by varying the speed of the rotator (and hence the time it takes for a product to move from the disk to the ring), determine the half-life of the intermediates.

The corrosion researcher may be interested in following oxidation reactions occurring at the disk by setting the ring to a potential that allows selection of specific species and oxidation states. The presence of a surface interaction such as a filming amine inhibitor may be observed using a bi-potentiostat and a ring-disk electrode. The electrochemical mechanisms occurring during corrosion can also be studied using a bi-potentiostat.

1.2. FEATURES

1. Four-electrode potentiostat.
2. Can be used as a three-electrode potentiostat.
3. May be used in galvanostat mode.
4. Current-to-voltage converter circuits to give output signal voltages proportional to the electrode currents.
5. F.E.T. amplifiers for measuring electrode voltages.
6. Set of internal resistors can be switched in place of the external electrodes.
7. Outputs protected against short circuits.
8. Overload indicator.
9. Auxiliary input jacks for applying an external voltage or program to either or both working electrodes.
10. Calibrated adjustable offset voltages which can be applied independently to the two working electrodes.
11. Summing circuits which will sum all electrode input signal voltages, apply sum to the electrode, and provide an output voltage signal for recording.
12. Dual range, controlled-scan sweep generator whose output voltage can be applied to either or both working electrodes.
13. Provision to set sweep to stop at a given voltage.

1.3. INITIAL INSPECTION

The bi-potentiostat should be inspected for shipping damage immediately after unpacking. If any damage is found, please notify the carrier and Princeton Applied Research. Save the shipping container for possible inspection by the carrier.

1.4. SAFETY CONSIDERATIONS

The Model 366A Bi-Potentiostat has been supplied in a safe condition. This manual contains some information and warnings that have to be followed by the user to ensure safe operation and to keep the apparatus in a safe condition. The bi-potentiostat has been designed for indoor use.

Warning!

The protective grounding could be rendered ineffective in damaged apparatus. Damaged apparatus should not be operated until its safety has been verified by qualified service personnel. Damaged apparatus should be tagged to indicate to a potential user that it may be unsafe and that it should not be operated.

As defined in IEC Publication 348, Safety Requirements for Electronic Measuring Apparatus, the Model 366A Bi-Potentiostat is Class I apparatus, that is, apparatus that depends on connection to a protective conductor to earth ground for equipment and operator safety. Before any other connection is made to the apparatus, the protective earth terminal must be connected to a protective conductor. The protective connection is made via the earth ground prong of the Model 366's power cord plug. This plug must only be inserted into a socket outlet provided with the required earth ground contact. The protective action must not be negated by the use of an extension cord without a protective conductor, by use of a plug adapter that doesn't maintain earth ground continuity, or by any other means.

In many parts of the world, commonly used power plugs and sockets differ from those in general use in the United States. If the power cord plug is not compatible with the available power sockets, the power cord should be replaced with an approved type of compatible design.

Warning!

If it is necessary to replace the power cord, the replacement cord must have the same polarity as the original. Otherwise a safety hazard from electrical shock, which could result in personnel injury or death, might result.

The wires in the supplied power cord are color-coded to maintain the correct polarity relationships. Whatever the actual plug configuration, the black wire should be the line or active conductor (also called "live" or "hot"), the white wire should be neutral, and the green wire should be earth ground.

1.5. POWER VOLTAGE SELECTION

The Model 366A bi-potentiostat can operate from either of two different voltage ranges. Instruments are ordinarily shipped set up for operation with the power line voltage available in the country in which they are to be used.

Before plugging in the power cord, make sure that the instrument is set for the voltage of the ac power line supply.

Caution!

The bi-potentiostat may be damaged if it is set for operation from 120 V ac and turned on with 240 V ac applied to the power input connector.

The bi-potentiostat is set for use with the line voltage available by changing the position of the removable voltage selector card inside the power entry module on the rear panel. If necessary, the change from one input voltage range to another can be accomplished in the field. **Changing the voltage range or changing the line fuse should only be done by a qualified service technician, and then only with the instrument disconnected from all sources of power.** A detailed discussion of how to check and, if necessary, change the input voltage setting follows.

Note the clear plastic door next to the power cord connector at the rear of the instrument. When the power cord is disconnected from the rear-panel connector, the plastic door is free to slide to the left, giving access to the fuse and to the voltage selector circuit card.

The voltage selector card can be inserted in either of two different positions, according to the power line voltage available. In either position, a number is visible on the upper surface of the card. This number indicates the selected nominal line voltage. When the number 120 is visible, the bi-potentiostat is set for power input voltages between 100 and 125 VAC. A setting of 240 is used for voltages between 200 and 250 VAC.

If the number showing on the card is incorrect for the prevailing line voltage, the card will have to be repositioned. To change the voltage setting:

1. Disconnect the power cord from the power entry module on the rear panel.
2. Slide the clear plastic door to the left.
3. Use pliers to carefully remove the the voltage selector card.
4. With the card removed, both numbers 120 and 240 are visible on it. Turn the card so the number indicating the correct operating voltage (120 for 100 VAC to 125 VAC; 240 for 200 VAC to 250 VAC) will remain visible when the card is replaced.
5. Reinsert the card into its connector with the desired operating voltage number visible. Be sure the board is securely seated.
6. Remove the fuse and check its rating. When the lever labeled FUSE PULL is rotated out and towards the left, the fuse will lift so that it can be easily removed. Use a slow-blow fuse rated at 3A. Make sure that only fuses with the required current rating and of the specified type are used for replacement.
7. When the proper fuse has been installed, slide the plastic door back over the fuse compartment and reconnect the power cord.

1.6. LINE FUSE REPLACEMENT

If your equipment will not operate, first check the fuse. Remove the power cord, slide the clear plastic door to the left, and use the PULL FUSE lever to remove the fuse. If the fuse is bad, replace it with a 3 amp slow-blow fuse after checking for the cause of the blown fuse. Slide the clear door back over the fuse compartment and plug the power cord back into the module.

1.7. SERVICE

This is an operating manual only and contains no service information. Users should note that the Model 366A is very difficult to service in the field; special fixtures and services are required that are not readily obtainable except at the factory or at certain affiliate facilities. Contact the factory service department or the affiliate in your area for additional service information.

There are no operator serviceable parts inside. Refer servicing to qualified personnel.

Chapter 4 describes troubleshooting procedures to determine whether problems that could be encountered during experiments are caused by the test setup or by a possible failure in the bi-potentiostat.

1.8. GENERAL DESCRIPTION

1.8.1. Sweep Generator

The dual-range sweep generator may be used to supply a sweep or scan signal to the electrodes. Particular attention was given to the design so that an operator will have complete flexibility in adjusting, sweeping, or stopping the sweep at any point in a particular cycle. Figure 1 shows the front panel jacks and controls of the Model 366A Bi-Potentiostat.

This is a true sweep generator in that period or frequency is not controlled, but rather the rate of sweep and the upper and lower limit of the sweep are the controlled factors. The two limits can be a few millivolts apart or up to four volts apart; these limits can be set both positive, both negative, or one positive and one negative.

In repetitive sweep, the upper and lower limits of sweep are independently adjustable between ± 9.999 V. The output signal sweeps between the high and low limits at the set sweep rate. The sweep can be stopped and held at any point, then started in either direction from the stop point at the discretion of the operator. In normal operation the sweep generator is free running. If desired, the sweep generator can be set to automatically stop at either end of the sweep. The voltage will hold at that point until the sweep circuit is started again.

1.8.2. Potentiostat

The potential control or potentiostat section is designed to be versatile and reliable while maintaining simplicity of operation. The potential is controlled independently of the current flowing in the cell; the potential applied to one electrode will not affect the potential or current of the other electrode. The rise time of the amplifiers in the bi-potentiostat is 0.5 volts per microsecond.

The Model 366A has a current output capability of 1 amp with a compliance voltage of ± 10 volts. The outputs are current limited to prevent damage to the bi-potentiostat in the event of a short circuit to DC common.

The bi-potentiostat features a current-to-voltage converting system for each working electrode. This circuitry produces a voltage output proportional to the electrode current to facilitate connection to external instruments, such as X-Y recorders or the A/D interfaces in a computer-controlled system. The scale factor of each current-to-voltage converter is set on a 16 position rotary switch, providing ranges from 1 microamp per volt to 100 milliamps per volt for each electrode.

Applying an offset voltage to an electrode is easily accomplished by use of a toggle switch and a four-digit pushbutton switch, allowing a range of ± 9.999 V accurate to $\pm 0.05\%$. The offsets are independently adjustable for each electrode.

The sweep generator output may be applied to either or both electrodes by actuation of the appropriate toggle switch(s). A signal from an external source, such as a function generator or a computer controller, may be applied to either or both electrodes by use of the input jacks in each electrode control section.

All front panel connections are made to the Model 366A via banana jacks except the reference electrode input, which utilizes a BNC shielded connector. There is also a ground jack on the front panel which is connected to the Model 366A case and to the ground connection of the power cord. This permits easy connection of DC common to the case and in turn to earth ground which, in some systems, may be advantageous to reduce electrical noise.

Output jack I1-I2 provides a voltage proportional to the difference between the currents flowing in the two electrodes, allowing measurements where one can subtract out background signals in identical electrodes.

Whenever one of the amplifiers in the 366A is nearing saturation (output > 10 V), the overload indicator lights to indicate a possible measurement error. The circuits continue to function even though the indicator is on.

To use the Model 366A as a 3-electrode potentiostat, it is not necessary to make any connections to the K2 electrode circuit.

1.8.3. Galvanostat

The K1 or disk electrode can be set to a galvanostat mode. In this mode, the signal voltage applied to the K1 input is converted to a current determined by the setting of the CURRENT CONVERTER switch.

When the MODE switch of the Model 366A is switched from the position for potentiostatic operation (POT) to the position for galvanostatic operation (GAL), the operation of electrode K1 is switched from potential control to current control. The operation of electrode K2 remains as potential control regardless of the mode selected for K1. Galvanostatic control of the disk electrode of a rotating ring-disk electrode (RRDE), with potentiostatic control of the ring electrode, can be applied for quantitative analytical determinations of electroinactive species, by way of the so-called "diffusion layer titrations" (discussed in Chapter 2), and for the measurement of rate constants for pseudo second-order homogenous reactions. In the galvanostatic mode, the current in the disk electrode is proportional to the signal voltage input and can be monitored as a potential at terminal I1 just as is the case for potentiostatic operation. The factor for conversion of the measured potential to current values is indicated by the setting on CURRENT CONVERTER. The magnitude and polarity of the disk current can be adjusted by way of the OFFSET VOLTAGE and/or the sweep generator, keeping in mind the conversion factor indicated by the setting on CURRENT CONVERTER.

1.8.4. Voltmeter

In the upper left corner of the front panel is a 3½ digit voltmeter. It may be used to display the Sweep Generator output or the E1 or E2 voltages applied to the K1 and K2 electrodes. Alternatively, it can be used to display the current readings I1 and I2, measured at the K1 and K2 electrodes. Potentials are displayed directly in volts while current readings display as a fraction of the Current Converter setting, e.g., a reading of 0.5 on the 50 μ A setting corresponds to 25 μ A.

1.9. SPECIFICATIONS

Power

100 - 125 VAC or 200 - 250 VAC, selectable by voltage-selection card, 50/60 Hz

Weight

12 lb (5.5 kg)

Operating temperature

10 deg. C to 40 deg. C

Dimensions

17 in. W x 13 in. D x 7-1/2 in. H
(43 cm W x 33 cm D x 19 cm H)

Sweep rate

dual range: 0-99.99 mV/sec; 0-999.9 mV/sec;
set on four-digit pushbutton switches.

Electrode current

1 amp maximum

Offset voltage

±9.999 V, set on four-digit pushbutton switches.

Electrode voltage

±10 volts

Current converters

20 ranges from 0.1 microamp per volt to 200 milliamps per volt.

Input impedance of reference potential follower

10^{12} ohms

Amplifier response

0.5 volts per microsecond

Small-signal bandwidth

>10 KHz, -3 db typical

Internal "dummy" resistors (see Figure 14)

REF: 100K ohms

CE: 2K ohms

K1: 1K ohms

K2: 1K ohms

1.10. SWITCH AND POTENTIOMETER FUNCTIONS

AC POWER switch

Up: On.

Down: Off.

MODE switch

Right: Potentiostatic operation.

Left: Galvanostatic operation.

ELECTRODES switch

normal: Connects electrode jacks into circuit.

dummy: Connects a set of internal resistors into the circuit. See Specifications.

1.10.1. Sweep Generator Section

MANUAL switch

up: Sweeps in positive direction.

center: Has no effect on sweep output.

down: Sweeps in negative direction

AUTO switch

on (up): for automatic sweep operation.

hold (center): Sweep holds at the value at time of switching

zero (down): Sweep output is zero.

SWEEP RATE potentiometer and range select switch

A calibrated four-digit pushbutton switch and a 2-position toggle switch for adjusting the sweep rate.

UPPER and LOWER LIMIT switches and associated toggle switches

These four-digit pushbutton switches set the values of the upper limit and lower limit respectively; used in conjunction with the associated switches, which may be used to set the values to either polarity. **Note:** The "upper" value must be more positive than the "lower" value by at least 10 mV.

STOP AT LIMIT switch

Up: The unit will sweep to the upper limit and hold.

Center: The unit will cycle continuously between the upper and lower limits if AUTO switch is on.

Bottom: The unit will sweep to the lower limit and hold.

1.10.2. K1 and K2 Electrode Section

OFFSET VOLTAGE switch and associated toggle switch

The four-digit pushbutton switch sets the magnitude of the applied voltage.

Toggle switch in off (center) position: no effect on electrode.

Toggle switch in + (up) position: Positive polarity on electrode

Toggle switch in - (down) position: Negative polarity on electrode

SWEEP VOLTAGE toggle switch

on (up): Output of sweep generator is applied to the electrode.

off (down): No effect on electrode voltage.

CURRENT CONVERTER rotary switch

Sets the scale factor for converting volts on Jack "I" to actual current in the electrode.

1.11. JACK FUNCTIONS

Front Panel

All black jacks

DC common, not frame or earth ground connected.

SWEEP VOLTAGE

Output of the Sweep Generator; may be used independently of the electrodes section.

ELECTRODES group

CE: Counter electrode connection, low-impedance output.

K1: K1, disk, or working electrode connection, low impedance, held at virtual DC common voltage potential.

K2: K2, ring or second working electrode connection; low impedance.

REF: Reference electrode connection; high impedance input which measures the REF voltage without loading the system.

Binding Post

Case, earth ground connection; a convenient point for connecting DC common to earth ground, if so desired.

K1 (K2) ELECTRODE group

- IN (IN): A voltage input jack connected through an internal 10K ohm resistor to the summing point of the K1 (K2) section. This allows a voltage to be applied from an external source, such as a function generator. This voltage is summed with the voltages applied by the offset system and the sweep voltage system.
- E1 (E2): A voltage output jack, which is a voltage indication of the actual K1 (K2) electrode voltage with respect to the REF electrode. This is a buffered output.
- I1 (I2): A voltage output jack which is a voltage indication of the actual K1 (K2) electrode current; it is used in conjunction with the current converter switch to produce current values. For example, if 2.0 volts is measured at the I1 (I2) jack, and the K1 (K2) current converter switch is set to the 0.5 mA per volt range, the actual K1 (K2) current is 1.0 mA ($2V \times 0.5 \text{ mA/V}$).
- I1 - I2: A voltage output jack which is a voltage indication of the difference in currents flowing in the K1 and K2 electrodes. The current converter switches for K1 and K2 must be in the same range for this voltage to be a valid value.

Rear Panel

- K1, K2, GAL: These jacks operate as pairs and allow capacitors to be inserted into the circuit to slow the response and eliminate oscillations which may occur under certain conditions. See the following section on noise and oscillations.

1.12. NOISE AND OSCILLATIONS

The eight black banana jacks on the Model 366A front panel are circuit common, and are floating with respect to the Model 366A case. On some systems it may be necessary to connect one of the black banana jacks to earth ground to reduce noise in the system. A banana jack connected to the instrument's case is provided on the front panel for convenience.

The bi-potentiostat is equipped with a three-wire power cord. The case of the unit is electrically connected to the green wire in the power cord. As the green wire is also connected to the normal ground pin on the 3-prong plug, the case is connected to earth ground when the bi-potentiostat is plugged into a three-prong outlet with a good quality earth ground connection.

All cables connected to the Model 366A front panel, especially the electrode connections, should be kept as short as possible. The REF electrode jack presents a very high input impedance, and is therefore susceptible to picking up unwanted signals or noise. The Model 366A incorporates an insulated BNC connector for the REF electrode connection, allowing complete shielding of the REF input lead. The shield of the REF electrode connector is driven to the same voltage as the REF signal. Therefore, **do not ground the shield**. The shield should not be connected to any other point at the electrode end, so no current can flow in the shield.

It is suggested that no connections, other than to the actual electrodes, be made to the ELECTRODE jacks, particularly the REF jack.

The Model 366A is an analog system which relies on feedback for stable operation. There is the possibility, on certain systems, that the feedback may become phase shifted and cause the unit to oscillate. It is suggested that anytime an abnormal situation occurs on the Model 366A - including jumps in potential or current, or the overload indicator glowing for no apparent reason - an oscilloscope be used to observe the outputs.

If oscillations are evident, and the techniques noted previously do not eliminate the problem, there are six jacks on the back panel to which capacitance may be connected to slow the response of the Model 366. It is suggested that 0.001 to 0.1 μF be added to the K1 or K2 jack, or to both jacks. Various combinations should be tried, as experience will best dictate what should be used. The capacitors should be either film or ceramic, 30 volts minimum.

If problems are experienced in the galvanostatic mode of operation, there are two jacks on the rear panel for external compensation in that mode only. The above values are recommended.

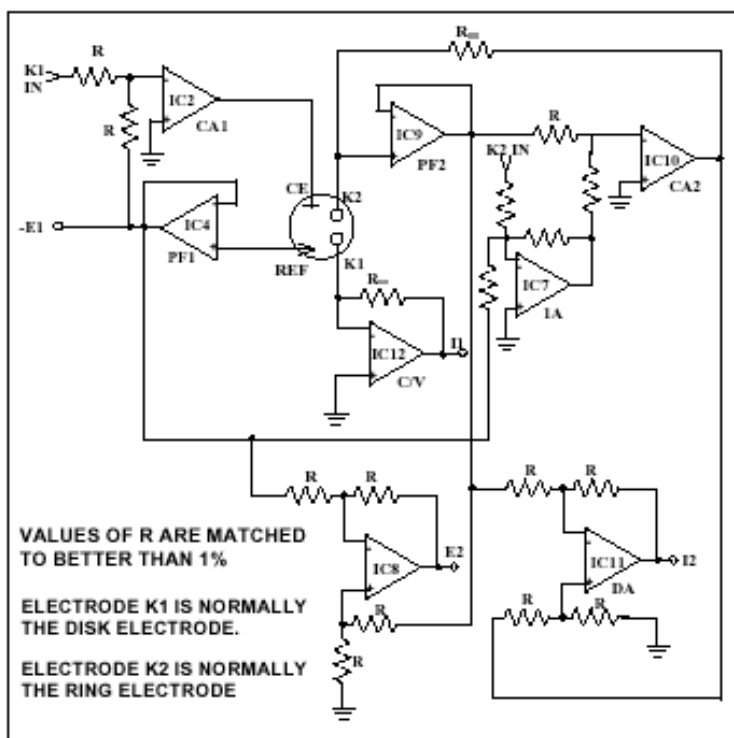


Fig. 2. SIMPLIFIED CIRCUIT DIAGRAM.

1.13. CIRCUIT DESCRIPTION

The first instrument for simultaneous and independent potentiostatic control of the ring and disk electrodes of a rotating ring-disk electrode was described by Napp, Johnson and Bruckenstein (*Anal. Chem.*, 39, 481 (1967)). The circuit of the Model 366A Bi-Potentiostat represents a substantial improvement over the first circuit in terms of capacity, response, and convenience. A brief analysis of the circuit is given here based on the simplified circuit diagram shown in Figure 2. Figure 3 shows the component layout of the Model 366A Bi-Potentiostat.

The circuitry for the potentiostatic control of working electrode 1, K1, consists of the potential follower PF1 and control amplifier CA1, whose output is connected to the counter electrode CE, and the current-to-voltage amplifier C/V. Amplifier C/V maintains the potential of K1 at virtual ground by means of its current feedback loop (R_{F1}). Amplifier CA1 maintains the difference in the potential between electrode K1, E_{K1} , and the reference electrode potential, E_{Ref} , equal to the signal potential, E_1 .

$$E_{K1} - E_{Ref} = E_1$$

In practice, the potential of K1 is measured directly at the output of PF1.

The circuitry required for potentiostatic control of the second working electrode, K2, consists of the potential follower PF1, the inverter amplifier IA, the control amplifier CA2, and the potential follower PF2. Amplifier CA2 functions by means of the current loop (R_{F2}) maintaining the value of the potential difference between electrode K2, E_{K2} , and the potential of the reference electrode, E_{Ref} , equal to minus the signal potential, E_2 .

$$E_{K2} - E_{Ref} = - E_2$$

Hence, the potential of the electrodes K1 and K2 may be controlled independently of each other. Because the current loop for amplifier CA2 includes electrode K1, it appears at first glance that the independent control of the current through electrode K1 has been destroyed. However, amplifier CA1 operates to maintain the equality $E_1 = E_{K1} - E_{Ref}$, and the counter electrode, CE, serves to complete the current loop for both indicating electrodes. In effect, the current through CE is the algebraic sum of the currents through K1 and K2.

There is an interaction between the two electrode signals in the uncompensated IR drop. Thus, the uncompensated IR drop between the reference electrode and K1 will cause an equivalent loss of potential control in K2. Although this error may be small in many cases, fairly large currents are encountered with convective electrodes, and the uncompensated IR drop must be kept at the lowest possible value by positioning the tip of the reference electrode very close to K1. The potential of K1, as measured at PF1, includes the error resulting from the uncompensated IR drop. When the Model 366A Bi-Potentiostat is used with ring-disk electrodes, K1 is usually the disk electrode and K2 is the ring electrode.

2. THEORY

2.1. THE DIFFUSION LAYER

Transport of an analyte within a solution can occur by the mechanisms of convection, diffusion and migration. Convective mass transport is the result of physical displacement of the solution caused by stirring. Diffusion is the transport of analyte from a location of high concentration to a location of lower concentration and occurs at a rate proportional to the concentration gradient. Migration is the transport of ionic analyte in response to an electrical potential gradient within the solution. The contribution of migration to the total rate of mass transport can be made negligible by addition of an inert electrolyte to the solution at a concentration much larger (>100 X) than that of the electroactive analyte. Migration will be assumed negligible for the remainder of this discussion.

The region adjacent to the surface of an electrode rotating in a solution can be considered as divided into two regions for the purpose of a qualitative description of mass transport to the electrode surface. For practical fluids having a finite viscosity, the solution contacting the electrode surface adheres and is described by the same velocity vectors as the electrode. Hence convection is negligible as a mechanism of mass transport within the adherent layer and diffusion alone is responsible for mass transport within this region. The layer of adherent solution wherein diffusion is the predominant mechanism of mass transport is called the *diffusion layer*. The thickness of the diffusion layer, measured perpendicular to the electrode surface, is given the symbol δ . In the region of the bulk solution beyond the diffusion layer, agitation (mixing) of the solution is eminent and convection predominates as the mechanism for mass transport. This model usefully describes the mass transport mechanism, even though there is not a sharp dividing line between the diffusion layer and the bulk convective region. In summary: Convection is responsible for bringing analyte from the bulk of the solution to the diffusion layer, and diffusion brings the analyte across the diffusion layer to the electrode surface.

For a constant rate of stirring, the faradaic current in the electrode is independent of time (steady state). A semiquantitative relationship between electrode current, I , and δ was given by Nernst in 1904. According to the law of Faraday, I is related to the flux of analyte, N , by Equation 1.

$$I = nFN \quad (1)$$

where

n = equiv/mole
 F = 96486.6 coul/equiv
 N = moles/sec

The flux at the electrode surface is related to the concentration gradient of the analyte measured at the electrode surface as given by Fick's law of diffusion in Equation 2.

$$N = AD(dC/dx)_{x=0} \quad (2)$$

where

A = area, cm^2
 D = diffusion coefficient, cm^2/sec
 C = concentration, mole/cm^3
 x = distance, cm

Nernst assumed a linear concentration gradient across the diffusion layer and approximated the gradient as given by Equation 3.

$$(dC/dx)_{x=0} = (C_{x=\delta} - C_{x=0})/\delta \quad (3)$$

The concentration of analyte at $x = \delta$ is virtually equal to the analyte concentration in the solution bulk, C^b . When the electrode potential is made sufficiently large relative to the standard reduction potential so $C_{x=0}$ approaches zero, I approaches a limiting value, I_l , as given by Equation 4.

$$\lim_{C_{x=0} \rightarrow 0} I = I_l = nFADC^b/\delta \quad (4)$$

The numerical value of δ in Equation 4 is a kind of calibrating factor and is observed to be inversely dependent on the rate of electrode rotation.

2.2. THE ROTATING DISK ELECTRODE

In the third decade of this century, V.G. Levich and coworkers made great progress in combining the mathematical equations previously developed describing fluid dynamics at submerged surfaces with consideration of the rate of electrolysis at electrodes of different geometries (*Physicochemical Hydrodynamics*, Prentice Hall, 1962). One of the electrode systems described by Levich is the rotating disk electrode shown in Figure 4.

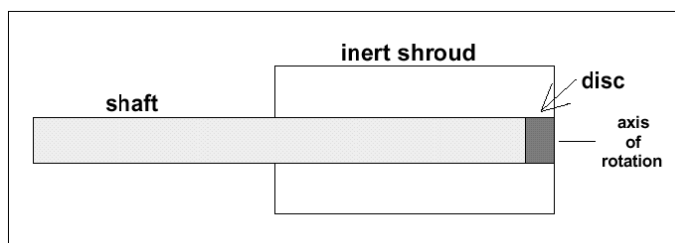


Fig. 4. CROSS-SECTIONAL DIAGRAM OF A ROTATING ELECTRODE.

The rotating disk electrode is constructed from a disk of the chosen electrode material mounted on the end of a metal (e.g., stainless steel or brass) shaft. The shaft and disk are covered by a cylindrical shroud of inert material (e.g., Kel-F, Teflon, epoxy, etc.) as shown in Figure 4. The shroud has two functions: (1) It prevents contact between the electrolytic solution and the metal shaft and disk edge; (2) The end surface of the disk is extended for full development of fluid flow patterns near the disk electrode.

In use, the disk electrode is rotated in a solution of electrolyte about an axis perpendicular to and passing through the center of the disk surface. The velocity of rotation must be precisely controlled to within 1%. The rotator is normally constructed with a synchronous motor or a variable speed motor controlled by a feedback system monitoring the rotational velocity. The complexities of constructing the electrode and rotator are sufficiently great that purchase of the equipment is recommended over in-house construction.

As a result of electrode rotation, a layer of solution at the disk surface adheres and rotates at an angular velocity equal to that of the electrode. Solution at some finite distance from the disk, Δx , is also rotating though not at the velocity of the electrode. The centrifugal force upon this fluid causes it to move in a radial direction. The radial fluid displacement is compensated by an axial fluid flow, as shown in the pictorial representation of the flow patterns in Figure 5.

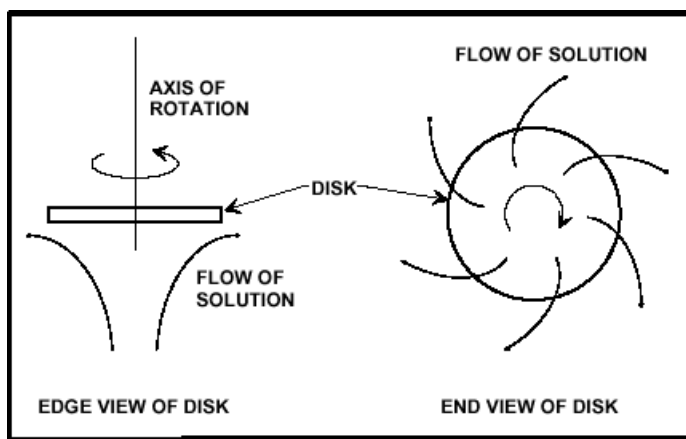


Fig. 5. FLUID FLOW PATTERNS AT ROTATING-DISK ELECTRODE.

The rate of electrode rotation can be easily maintained at a constant value and, consequently, the fluid velocity in the vicinity of the electrode surface is constant. The result is that the electrochemical current resulting from the mass transport of electroactive material from the bulk of the solution to the electrode and the subsequent electrode reaction is constant. The exact functional expression describing δ and its relationship to the rate of electrode rotation can only be obtained from a consideration of the hydrodynamic patterns of fluid flow around the electrode. A brief account of that consideration is given here.

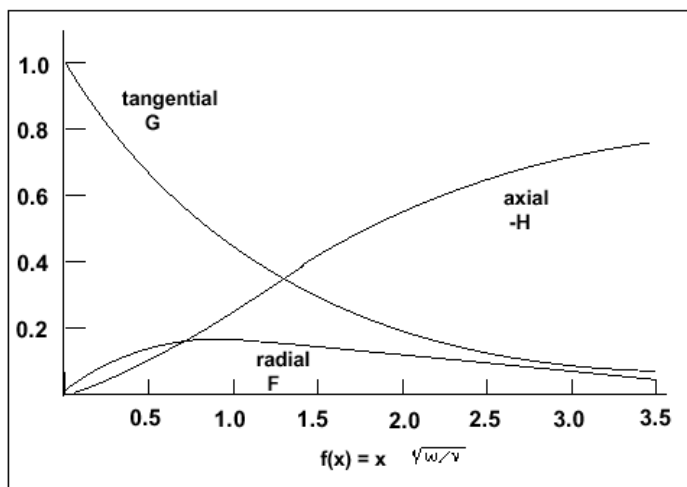


Fig. 6. TANGENTIAL, AXIAL, AND RADIAL VELOCITIES AS A FUNCTION OF THE NORMAL DISTANCE FROM THE ELECTRODE SURFACE.

The Navier-Stokes equations which describe the convective flow at the surface of a rotating electrode were first solved independent of any electrochemical application. The tangential (θ), radial (r), and axial (x) flow velocities, v_θ , v_r , and v_x , were solved as series functions and are given in Equations 5-11.

$$v_\theta = r\omega G(\xi) \quad (\text{tangential}) \quad (5)$$

$$v_r = r\omega F(\xi) \quad (\text{radial}) \quad (6)$$

$$v_x = (\nu\omega)^{1/2} H(\xi) \quad (\text{axial}) \quad (7)$$

where

$$\xi = (\omega/\nu)^{1/2} x \quad (8)$$

and

$$G(\xi) = 1 + b\xi + 1/3a\xi^3 + 1/2(ab - 1)\xi^4 - 1/15b\xi^5 - \dots \quad (9)$$

$$F(\xi) = a\xi - 1/2\xi^2 - 1/3b\xi^3 - 1/12b^2\xi^4 - \dots \quad (10)$$

$$H(\xi) = -a\xi^2 + 1/3\xi^3 + 1/6b\xi^4 + 1/30b^2\xi^5 + \dots \quad (11)$$

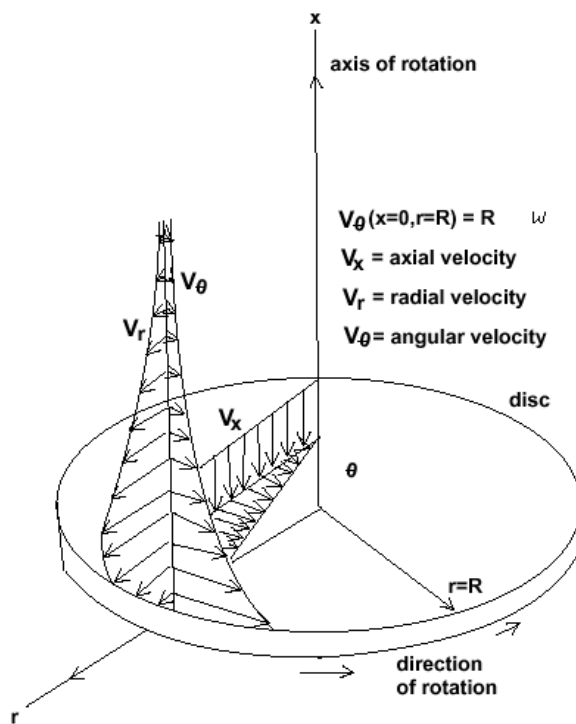


Fig. 7. DIAGRAM OF AXIAL RADIAL, AND ANGULAR FLUID VELOCITY VECTORS NEAR A DISK ROTATING IN VISCOUS FLUID.

In Equations 9-11, $a = 0.510$ and $b = -0.616$. In all of the equations, ν = kinematic viscosity of the fluid and ω = angular velocity of electrode rotation. The velocity functions are shown plotted versus the dimensionless function $x(\omega/\nu)^{1/2}$ in Figure 6 and are diagrammed in Figure 7.

For small values of ξ , i.e., near the electrode surface, all but the first terms may be dropped from the series solutions. Thus

$$r_\theta = r\omega \quad (12)$$

$$v_r = 0.510 r x (\omega^3/\nu)^{1/2} \quad (13)$$

$$v_x = -0.510 x^2 (\omega^3/\nu)^{1/2} \quad (14)$$

The thickness of the solution layer near the electrode in which the axial flow has reached 80% of its maximum value is called the hydrodynamic layer, δ_0 . Essentially, beyond δ_0 the angular and radial velocity components are nonexistent.

$$\delta_0 = 3.6 (\nu/\omega)^{1/2} \quad (15)$$

The equation of convective-diffusional mass transport as it applies to the rotating disk electrode is given below.

$$(\partial C/\partial t) + v_r(\partial C/\partial r) + v_x(\partial C/\partial x) = D(\partial^2 C/\partial x^2) \quad (16)$$

Solution of the equation above for a rotating electrode is greatly simplified if the term $\partial C/\partial t$ is negligible. This is valid if the rate of rotation is constant and steady-state conditions apply. Further simplification results because the electrode material is an excellent conductor and the electrical potential across the surface is uniform. Furthermore, the value of C at a distance $x = \delta$ is uniform and as a result, $\partial C/\partial r = 0$. This is frequently called the *uniform accessibility condition*.

Equation 16 is solved with the use of the following boundary conditions:

- (i) limiting disk current, i.e., $C_{x=0} = 0$ and $I = I_{l,d}$
- (ii) for $x \rightarrow \infty$, $C_{x=\infty} = C^b$
- (iii) from Faraday's and Fick's laws,

$$(\partial C/\partial x)_{x=0} = I/nFAD$$

The mathematical solution is

$$I_{l,d} = 0.62 nFAD^{2/3} \nu^{-1/6} \omega^{1/2} C^b \quad (17)$$

where

$I_{l,d}$ = limiting disk current, mA;

C^b = bulk concentration of electroactive species, M;

A = area of disk electrode, cm²;

D = diffusion coefficient of electroactive species, cm²/sec;

ν = kinematic viscosity of solution, cm²/sec;

ω = angular velocity of electrode rotation, rad/sec.

Equation 17 is known as the Levich equation.

Equation 17 is not valid for $\omega \rightarrow \infty$ because the derivation assumes laminar (i.e., nonturbulent) fluid flow at the electrode surface. The onset of turbulence occurs for rotational velocities characterized by a Reynolds number, N_{Re} , of approximately 10^5 . N_{Re} is calculated by Equation 18

$$N_{Re} = r^2\omega/\nu \quad (18)$$

where r is the total radius of the electrode plus the non-active shroud. For a typical electrode with $r = 1$ cm and $\nu = 10^{-2}$ cm²/sec, the onset of turbulence is expected at $\omega = 6 \times 10^4$ rad/sec (10^4 rev/min).

Gregory and Riddiford [*J. Chem. Soc.*, 3756 (1956)] compared experimental values of $I_{l,d}$, for systems with electroactive species of known D , to values predicted by the Levich equation. The experimental values were approximately 5% greater for $D/\nu = 4 \times 10^{-3}$. The Levich derivation was examined and the error concluded to result from the omission of terms other than the first in Equation 11 describing the axial fluid velocity. Gregory and Riddiford rederived the equation for $I_{l,d}$ including the second term in Equation 11 with the result given by Equation 19.

$$I_{l,d} = \{1/[1.61 + 0.57(D/\nu)^{0.36}]\} nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C^b \quad (19)$$

This correction brings the predicted value to within 1% for D/ν as large as 4×10^{-3} . Note that for small D/ν , the numerical coefficient is 0.62 as predicted by Levich.

2.3. THE ROTATING RING-DISK ELECTRODE (RRDE)

A ring-disk electrode is shown in Figure 8. In the ring-disk electrode, an annular electrode (ring) is positioned symmetrically about the disk and the surfaces of the ring and the disk electrodes are coplanar. The current in the ring electrode is influenced by reactions occurring at the disk electrode which increase or decrease the concentration of electroactive species in the radial flow stream.

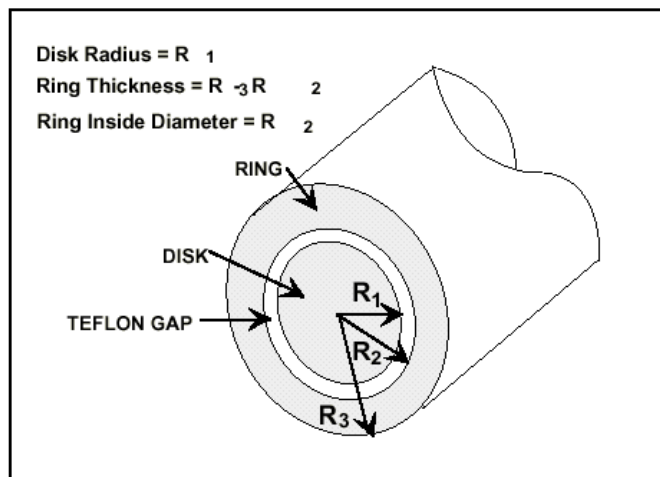


Fig. 8. ROTATING RING-DISK ELECTRODE.

To obtain explicit equations predicting the ring current, the equation of mass transport must be solved including the term for radial convection, $v_r(\partial C/\partial r)$. In the absence of any reaction at the disk electrode, the mass transport-limited faradaic current in the ring electrode is given by Equation 20.

$$I_{1,r} = 0.62nF\pi(R_3^3 - R_2^3)^{2/3}D^{2/3}\omega^{1/2}\nu^{-1/6}C^b \quad (20)$$

The ratio $I_{1,r}/I_{1,d}$ is a constant for any given electrode design and is determined solely by the geometry of the electrode.

$$\begin{aligned} I_{1,r}/I_{1,d} &= (R_3^3 - R_2^3)^{2/3}/R_1^2 \\ &= [(R_3/R_1)^3 - (R_2/R_1)^3]^{2/3} \\ &= \beta^{2/3} \end{aligned} \quad (21)$$

There is no particular advantage in the use of a ring electrode rather than a disk electrode for direct electroanalytical determinations. The opportunities provided by the ring electrode design are only the result of its use in conjunction with a disk electrode.

Diffusion and convection, both axial and radial, near the surface of a rotating ring-disk electrode (RRDE) results in products of a reaction at disk surface being transported to the vicinity of the ring electrode where they may undergo further reaction. The rate of mass transport is surprisingly large; for a 0.005 to 0.010 cm separation of the ring and disk electrodes, unstable disk reaction products with half lives as short as 1 msec can be studied at the ring electrode if the electrode rotational velocity is approximately 10,000 rev/min. The fraction of species produced at the disk electrode that is capable of reacting at the ring electrode is called the theoretical collection efficiency, N_0 . N_0 is a function only of the geometry of the RRDE and is independent of rotation velocity as given by Equation 22.

$$\begin{aligned} N_0 &= 1 - F(\alpha/\beta) + \beta^{2/3}[1 - F(\alpha)] \\ &\quad - (1 + \alpha + \beta)^{2/3} \{1 - F[\alpha/\beta(1 + \alpha + \beta)]\} \end{aligned} \quad (22)$$

where

$$\begin{aligned} F(x) &= \int_0^x (3^{1/2}/2\pi) \frac{dx}{[x^{2/3}(1+x)]} \\ &= (3^{1/2}/4\pi) \ln [(1+x^{1/3})^3/(1+x)] \\ &\quad + 3/2\pi[\arctan \{(2x^{1/3} - 1)/3^{1/2}\}] + 1/4 \end{aligned} \quad (23)$$

Values of N_0 for typical values of radius ratios are given in Table 1.

The limiting current in the ring of a RRDE when no reaction occurs at the disk electrode is given by Equation 21. In Equation 24, $I_{1,d}$ is the limiting current which could flow in the disk electrode as predicted by Equation 17.

$$I_{1,r} = \beta^{2/3}I_{1,d} \quad (24)$$

Since a portion of the species reacting at the ring electrode is transported to the ring by a path which approaches the surface of the disk, potentiostating the disk electrode in the region of limiting current results in a decrease of the ring current from the value $I_{1,r}$. The extent of the decrease is $N_0 I_{1,d}$.

$$\begin{aligned} I_r &= I_{1,r} - N_0 I_{1,d} \\ &= \beta^{2/3} I_{1,d} - N_0 I_{1,d} \\ &= (\beta^{2/3} - N_0) I_{1,d} \end{aligned} \tag{25}$$

A shielding efficiency, S , is defined as the ratio of the ring electrode current observed when the disk electrode is at a potential for the mass transported-limited reaction and the ring electrode current when the disk electrode current is zero.

$$S = (\beta^{2/3} - N_0) I_{1,d} / \beta^{2/3} I_{1,d} = 1 - N_0 / \beta^{2/3} \tag{26}$$

2.4. SURFACE CONTROLLED ELECTRODE CURRENT

Current-potential (I-E) curves obtained for noble metal electrodes, such as platinum, are characterized by waves resulting from faradaic reactions which involve direct participation of the metal surface. These faradaic reactions are, in fact, limited in their extent by the number of metal atoms at the surface of the electrode and are described as being "surface controlled reactions." Surface-controlled reactions are much different than mass-transport controlled reactions which occur at a rate limited by the flux of the electroactive species at the electrode surface.

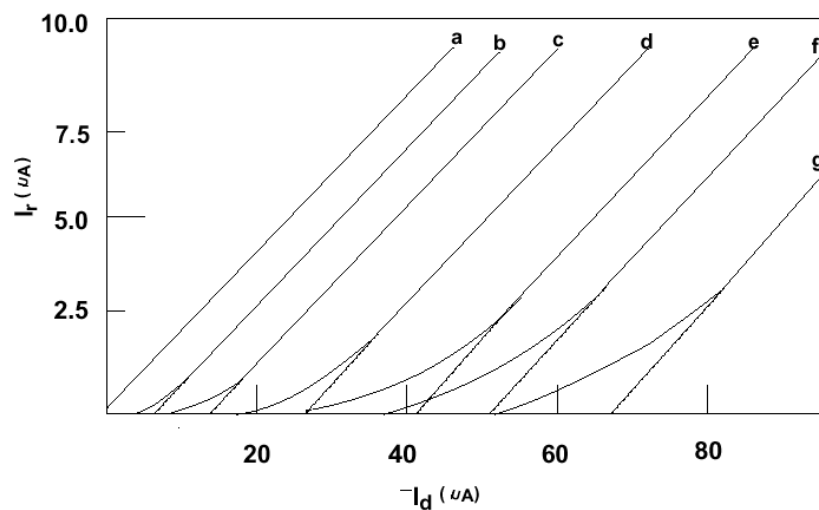
The most familiar surface-controlled reactions for platinum electrodes in aqueous solution are the anodic formation and cathodic dissolution of a thin film of platinum oxide at the electrode surface. When the potential of a Pt electrode in an aqueous solution is scanned in a positive direction, a wave corresponding to formation of PtOH and PtO is observed at $E > +0.5$ V versus SCE, for a solution pH of 1. The oxide film is very dense and protects the metal from further oxidation. The effectiveness of this film is apparent in the fact that Pt is known as a noble metal. The film of PtO is cathodically reduced by a surface-controlled reaction during the negative potential sweep. Much controversy exists regarding the electrochemistry of the oxide film. Because the film corresponds to more than one layer of Pt atoms, the oxidation state of Pt in the film is not definitely known. There is also disagreement whether the platinum oxide is reduced all the way to pure Pt during the negative potential sweep or to a semi-stable state such as PtOH.

Surface-controlled current peaks are also observed for Pt electrodes resulting from the reduction of H^+ to produce atomic H which is adsorbed to the Pt surface. Because there is energy gained by adsorption of H, these cathodic surface-controlled peaks are observed on the negative potential scan before the evolution of gaseous H_2 .

R_3/R_2	R_2/R_1								
	1.02	1.03	1.04	1.05	1.06	1.07	1.08	1.09	1.10
1.02	.1013	.0976	.0947	.0922	.0902	.0884	.0869	.0855	.0843
1.03	.1293	.1250	.1215	.1186	.1162	.1140	.1121	.1104	.1089
1.04	.1529	.1483	.1444	.1412	.1385	.1360	.1339	.1320	.1302
1.05	.1737	.1687	.1747	.1612	.1582	.1556	.1533	.1512	.1493
1.06	.1923	.1872	.1829	.1793	.1761	.1733	.1708	.1686	.1665
1.07	.2092	.2039	.1996	.1958	.1925	.1896	.1869	.1846	.1824
1.08	.2247	.2194	.2149	.2110	.2076	.2046	.2019	.1994	.1972
1.09	.2392	.2338	.2292	.2252	.2217	.2186	.2158	.2133	.2110
1.10	.2526	.2472	.2426	.2385	.2350	.2318	.2289	.2263	.2240
1.12	.2772	.2717	.2670	.2629	.2593	.2560	.2530	.2503	.2479
1.14	.2992	.2938	.2890	.2849	.2812	.2778	.2748	.2720	.2695
1.16	.3192	.3138	.3090	.3048	.3011	.2977	.2947	.2919	.2893
1.18	.3375	.3321	.3274	.3232	.3194	.3161	.3130	.3101	.3075
1.20	.3544	.3490	.3443	.3402	.3364	.3330	.3299	.3271	.3245
1.22	.3701	.3648	.3601	.3560	.3523	.3489	.3458	.3429	.3403
1.24	.3848	.3795	.3749	.3708	.3671	.3637	.3606	.3577	.3551
1.26	.3985	.3933	.3887	.3847	.3810	.3776	.3745	.3717	.3691
1.28	.4115	.4063	.4018	.3977	.3941	.3907	.3877	.3849	.3822
1.30	.4237	.4186	.4141	.4101	.4065	.4032	.4001	.3973	.3947
1.32	.4353	.4302	.4258	.4218	.4183	.4150	.4119	.4092	.4066
1.34	.4463	.4413	.4369	.4330	.4294	.4262	.4232	.4204	.4178
1.36	.4567	.4518	.4475	.4436	.4401	.4369	.4339	.4311	.4286
1.38	.4667	.4619	.4576	.4538	.4503	.4471	.4441	.4414	.4389
1.40	.4762	.4715	.4673	.4635	.4600	.4568	.4539	.4512	.4487

Table 1. VALUES OF COLLECTION EFFICIENCY FOR TYPICAL RADIUS RATIOS.

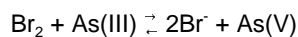
The reason that two peaks rather than one peak are observed for the formation of adsorbed H is a rather fascinating story. The Pt used for fabrication of electrodes (whether in the form of a wire or plate) is polycrystalline. The free energy of adsorption of atomic H and, therefore, the potential for the corresponding current peak is different for each crystal plane. Measurements have revealed that three crystal planes are present at the surface of polycrystalline Pt, but the values of the hydrogen adsorption energy for two of the three are very similar. Hence, only two peaks are clearly visible. Two anodic peaks are obtained on the positive potential sweep, for a Pt electrode bearing adsorbed H, corresponding to the anodic dissolution of the atomic H. The current-potential curve obtained for a Pt electrode in H_2SO_4 is shown in Figure 11.



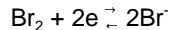
Disk electrode reaction (controlled current):



Solution reaction:



Ring electrode reaction (controlled potential):



$R_1 = 0.3886$ cm, $R_2 = 0.3986$ cm, and $R_3 = 0.4443$ cm;

$\omega = 21.1$ rad sec^{-1} ; 1.0 M $\text{H}_2\text{SO}_4 = 0.2$ M KBr supporting electrolyte; ring potential of 0.3 V vs. SCE.

Concentration of As(III):

- a. 0.0 μM
- b. 11.7 μM
- c. 23.4 μM
- d. 47.0 μM
- e. 70.5 μM
- f. 94.0 μM
- g. 117.0 μM

Plot of $(I_d)_{I_r=0}$ vs. $C_{\text{As(III)}}^b$ is linear with zero intercept and slope of $5.21 \times 10^5 \mu\text{A mole}^{-1} \text{L}$.

Figure 9. DIFFUSION-LAYER TITRATION CURVES.

By their nature, surface-controlled reactions proceed until the reaction of the electrode surface is complete and then the faradaic current drops to zero. Hence the quantity of charge, Q, corresponding to a surface-controlled reaction is a constant for a given electrode area.

Diagnostic evidence that a reaction is surface controlled is the observation that Q is independent of variations in the rate of solution stirring. Students of electroanalysis should be warned that there are many electrode reactions which have mixed control; a behavior which is surface-controlled for some conditions and mass-transport controlled for other conditions.

The fact that surface-controlled faradaic reactions are so common for noble metal electrodes places an interesting requirement on the methodology of electroanalysis. Surface-controlled reactions are seldom utilized for quantitative analysis and they constitute an interference in analytical voltammetry.

The mass-transport controlled faradaic current for the analyte must be measured in a manner which minimizes or accurately corrects for the contribution of the surface-controlled reaction. One method of minimizing the surface-controlled current is the recording of I - E curves at a very slow potential scan rate. Since the total charge passed between two potential limits is fixed for a surface-controlled reaction, the corresponding current will be inversely proportional to the rate at which the electrode potential is scanned over the potential range of the reaction.

2.5. DIFFUSION LAYER TITRATIONS

Galvanostatic control of the disk electrode of a rotating ring-disk electrode, with potentiostatic control of the ring electrode, can be applied for quantitative analytical determinations of electroinactive species using diffusion layer titrations. In the galvanostatic mode, the current in the disk electrode is proportional to the signal voltage input and can be monitored as a potential by the Model 366A. Galvanostatic operation of this unit is described in Chapter 1, pages 2 and 3.

The name "diffusion layer titration" is given to a sensitive analytical technique for the quantitative determination of electroinactive analytes [S. Bruckenstein and D. C. Johnson, *Anal. Chem.*, 36, 2186 (1964)]. In this technique, a reagent is generated under controlled current at the disk of a rotating ring-disk electrode. The reagent reacts homogeneously with the analyte in the region of the diffusion layer and any excess unreacted reagent is detected amperometrically at the ring electrode.

The theory of diffusion layer titrations was developed by Albery [W. J. Albery, S. Bruckenstein and D. C. Johnson, *Trans. Faraday Soc.*, 62, 1938 (1966)] and will be only briefly summarized here.

Consider the sequence of reactions shown below.

Disk electrode (controlled current): $A \pm ne \rightarrow B$

Solution reaction (diffusion layer): $B + P \xrightarrow{k} A + Q$

Ring electrode (controlled potential): $B \mp ne \rightarrow A$

The boundary conditions for these reactions are summarized as follows: The bulk concentration of A is large compared to P ; the back reaction for the solution reaction is negligible; the surface concentration of B at the ring electrode is zero; i.e., limiting ring current for detection of excess B . Of experimental importance are plots of I_r versus I_d ; typical curves for the diffusion layer titration of $As(III)$ in 1.0 M H_2SO_4 by electrogenerated Br_2 are shown in Figure 9. For $C_{As(III)}^b = 0$, the slope of the I_r - I_d plot is $-N_0$ as predicted by equation 22 (see curve a in Figure 9). For $C_{As(III)}^b > 0$, $I_r = 0$ for all values of I_d for which the flux of B does not exceed the flux of P to the region defined by the area πR_2^2 . With increasing I_d , I_r increases from a zero value with a nonlinear dependence on I_d . This curved portion of the I_r - I_d plot corresponds to the situation wherein the

reaction between B and P at $x = 0$ is occurring in the region of the ring electrode. For large I_d , when the flux of B far exceeds the flux of P, the I_r - I_d curve is described by equation 28

$$I_r = -N_0 I_d - MB^{2/3} \quad (28)$$

where M is related to the flux of P as given by equation 29.

$$M = 1.95R_1^2 nFD^{2/3} \omega^{1/2} \nu^{-1/6} C_P^b \quad (29)$$

Note that the slope of the I_r - I_d plot is $-N_0$ (see curve b of Figure 9) for large I_d . Extrapolation of the linear portion of the I_r - I_d curve to $I_r = 0$ defines a value of I_d which is a linear function of the flux of P as given by equation 30.

$$(I_d)_{I_r=0} = -MB^{2/3}/N_0 \quad (30)$$

A plot of $(I_d)_{I_r=0}$ versus C_P^b is predicted to be linear for constant rotational velocity. Conversely, a plot of $(I_d)_{I_r=0}$ versus $\omega^{1/2}$ is linear for constant C_P^b .

Albery has criticized the use of plots of equation 30 as described above for quantitative analysis because a slight misjudgment in the graphical extrapolation can lead to serious error in the value determined for $(I_d)_{I_r=0}$ [*Trans. Faraday Soc.*, 62, 1938 (1966)]. An alternative method of treating the data is described in the original literature.

The curved portion of I_r - I_d curves obtained for diffusion layer titrations can be analyzed to obtain information regarding the rate of the homogeneous reaction. Consider first the example of a diffusion controlled solution reaction ($k \rightarrow \infty$). The observed I_r remains zero for increasing I_d until the radial coordinate (r) of the reaction zone of B with P, at $x = 0$, just reaches the inner edge of the ring electrode ($r = R_2$). Now imagine that I_d is held constant for this condition and the value of k for the solution reaction is considered to decrease. The reagent B penetrates beyond the region $r = R_2$ resulting in a non-zero value of I_r . The original literature (references 4-6 below) should be consulted for application of diffusion layer titrations for kinetic studies.

2.6. LITERATURE CITED AND FURTHER READING

1. V. G. Levich, *Physicochemical Hydrodynamics*, Eng. transl. by Scripta Technica, Inc., Prentice-Hall, Inc., Englewood Cliffs, NJ, 1962.
2. W. J. Albery and M. L. Hitchman, *Ring-disc Electrodes*, Clarendon Press, Oxford, 1971.
3. Yu. V. Pleskov and V. Yu. Filinovskii, *The Rotating Disc Electrode*, Eng. transl. by H. S. Wroblowa, Consultants Bureau, New York, 1976.
4. W. J. Albery and S. Bruckenstein, *Trans. Faraday Soc.*, 62, 2584, 1966.
5. W. J. Albery, M. L. Hitchman, and J. Ulstrup, *Trans. Faraday Soc.*, 65, 1101, 1969.
6. S. Bruckenstein and D. C. Johnson, *J. Am. Chem. Soc.*, 90, 6592, 1968.
7. D. T. Napp, D. C. Johnson, and S. Bruckenstein, *Anal. Chem.*, 39, 481, 1967.
8. V. G. Levich, *Acta Physicochem. URSS*, 17, 257.
9. D. T. Napp, Ph.D. thesis, University of Minnesota, 1967.
10. D. F. Unterecker, Ph.D. thesis, State University of New York at Buffalo, 1973.
11. D. F. Unterecker, W. G. Sherwood, G. A. Martinchek, T. M. Reidhammer, and S. Bruckenstein, *Chem. Inst.* 6(3), 259-66, 1975.

3. ELEMENTARY EXPERIMENTS

3.1. EQUIPMENT AND SOLUTIONS

1. Model 366A Bi-Potentiostat.
2. Rotating platinum ring-disk electrode (disk electrode only used for Experiments A and B).
3. Electrode rotator, such as Princeton Applied Research Model 636.
4. X-Y recorder.
5. Digital voltmeter (optional).
6. Saturated calomel reference electrode (SCE).
7. Electrolysis cell with Luggin capillary, cover, and facilities for deaeration with dispersed nitrogen (see Figure 10).

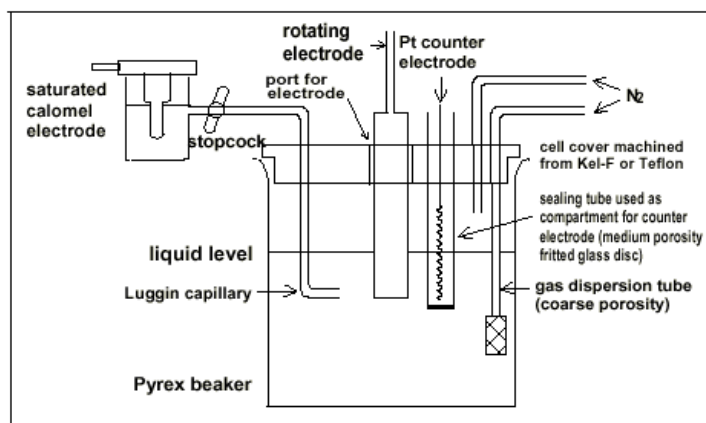


Fig. 10. DESIGN OF SIMPLE ELECTROLYSIS CELL.

8. Platinum counter electrode (15-cm length of 22-ga wire is sufficient).
9. 0.5 M H₂SO₄ (28 mL of reagent grade, concentrated acid per liter of solution).
10. 0.5 mM KI + 0.5 M H₂SO₄ (0.0830 g KI per liter; acidic solutions should be deaerated before addition of KI to prevent oxidation of I⁻ to I₂ by dissolved oxygen).
11. Cylinder of compressed, purified nitrogen for deaeration of solutions.

3.2. EXPERIMENT A: RESIDUAL CURRENT-POTENTIAL CURVE FOR Pt ELECTRODES IN ACIDIC SOLUTIONS

In Experiment A, the current-potential (I-E) behavior of a Pt electrode will be observed in an acidic solution containing no added electroactive analyte. The observation of the residual I-E curve is the customary basis of testing rotating disk and ring-disk electrodes for capillary leakage of solution into the seal between the electrode and the surrounding insulating shroud.

1. Assemble the electrolysis cell and fill with 0.5 M H₂SO₄ to the appropriate level. (Note: All glass surfaces should be cleaned prior to use by soaking in hot HNO₃ followed by thorough rinsing with distilled water.) Fill the counter electrode and reference electrode chambers with 0.5 M H₂SO₄. The stopcock of the Luggin reference chamber should be wetted with the electrolyte to maintain ionic contact between the solution in the electrolysis cell and the SCE, but should be in the closed position to prevent rapid mixing of the solutions between the two chambers. The Luggin capillary tubing should be free of any entrapped gas bubbles as their presence will disrupt proper functioning of the bi-potentiostat.
2. Mount the RRDE securely in the rotator. Excessive force should not be applied to the Teflon shroud of the electrode as this may result in the slipping of the shroud along the metal shaft. Mount the electrolysis cell in a position so that the RRDE enters the cell through the electrode port and the end of the RRDE is submerged approximately 5 mm below the surface of the solution. The RRDE should be centered in the electrode port so the shroud of the RRDE does not rub against the cell cover.
3. Attach tubing from the N₂ cylinder to the gas dispersion tube. Pass N₂ through the dispersion tube for approximately 10 min to deaerate the solution in the electrolysis cell. The flow rate of the gas should be such that the solution is agitated vigorously by the gas bubbles but excessive splashing does not occur. Proceed with steps 4-6 during deaeration.
4. Set the controls of the Model 366A Bi-Potentiostat as indicated below.

<u>Section</u>	<u>Control</u>	<u>Position</u>
---	AC POWER	OFF
---	ELECTRODES	NORMAL
---	MODE	POT
SWEEP GENERATOR	MANUAL	Center position (off)
SWEEP GENERATOR	AUTO	ZERO
SWEEP GENERATOR	SWEEP RATE	33.3 mV per sec
SWEEP GENERATOR	UPPER	+1.40 V
SWEEP GENERATOR	LOWER	-0.25 V
SWEEP GENERATOR	STOP AT LIMIT	Center position (off)
K1 ELECTRODE	OFFSET VOLTAGE	Center position (off)
K1 ELECTRODE	SWEEP VOLTAGE	ON

<u>Section</u>	<u>Control</u>	<u>Position</u>
K1 ELECTRODE	CURRENT CONVERTER	0.2 mA per volt
K2 ELECTRODE	OFFSET VOLTAGE	Center position (off)
K2 ELECTRODE	SWEEP VOLTAGE	OFF
K2 ELECTRODE	CURRENT CONVERTER	20 mA per volt

5. Suggested settings for the X-Y recorder are given below.

X-axis sensitivity: 200 mV/in (100 mV/cm)

Y-axis sensitivity: 200 mV/in (100 mV/cm)

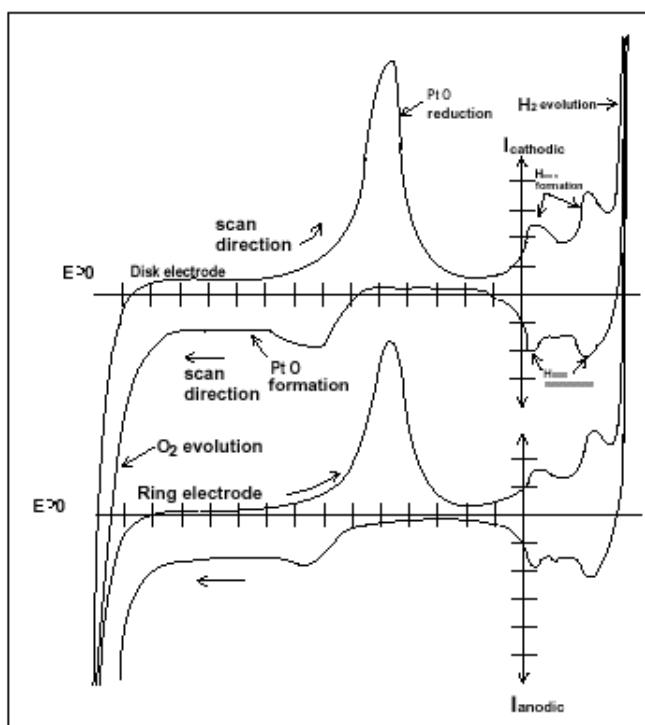
X-axis zero: as appropriate so entire scan of electrode voltage from -0.25 V to +1.40 V is accommodated on scale

Y-axis zero: center of scale

6. Make connections from the Model 366A Bi-Potentiostat to the RRDE and the X-Y recorder as indicated below.

<u>From Model 366A:</u>	<u>Connect to:</u>
CE ELECTRODE	Pt counter electrode
REF ELECTRODE	Saturated calomel electrode
K1 ELECTRODE	Contact for disk electrode of RRDE
(K2 ELECTRODE is not used in this experiment.)	
E1 jacks of K1 section	X-axis input on recorder
I1 jacks of K1 section	Y-axis input on recorder
(The black plug represents common potential on the Model 366A.)	
Digital voltmeter (if used)	Parallel with X-axis

7. When the solution in the electrolysis cell has been deaerated by the dispersion of N_2 , change the flow of N_2 to pass over the solution rather than through the solution. An atmosphere of N_2 must be maintained over the solution during experimentation to prevent entry of O_2 into the solution. The flow of N_2 over the solution should be at a rate so that the sound of the flowing gas is audible. Start the electrode rotating at 1600 rev/min. If N_2 bubbles adhere to the Pt surface of the RRDE, momentarily lower the electrolysis cell so the contact between the RRDE and solution is broken, then return the cell to its original position. Repeat this process, if necessary, until no bubbles adhere to the surface of the RRDE.
8. Turn the AC POWER switch of the Model 366A to the ON position. Also turn power switches for the digital voltmeter and X-Y recorder to the ON positions. The voltmeter should read 0.00 ± 0.01 V and the recorder pen should be in the zero position on both the X- and Y-axis. If these values are not observed, refer to the section on troubleshooting in Chapter 4.



Recorder:

X-axis sensitivity = 100 mV/cm

Y-axis sensitivity = 100 μ A/cm

ZERO position indicated by +

Potential sweep: rate = 33.3 mV/sec

range = -0.25 V to +1.40 V vs. SCE

sweep direction indicated by arrows

Current sensitivity: disk = 0.2 mA/V (20 μ A/cm)

ring = 50 μ A/V (5 μ A/cm)

RRDE speed = 1600 rev/min

Solution: 0.5 M H₂SO₄

Figure 11. RESIDUAL CURRENT-POTENTIAL CURVES AT PLATINUM DISK AND RING ELECTRODES.

- Place the MANUAL switch of the Model 366A momentarily in the UP position and place the AUTO switch in the ON position. The scan of the electrode potential will commence from 0.00 V, in the positive direction, and continue to scan between the limits of +1.40 V and -0.25 V so long as the AUTO switch is in the ON position. Allow the electrode potential to cycle several times (5 to 10) until the I-E curve is reproducible before recording the curve on the X-Y recorder. Adjustment of the sensitivity of the Y-axis may be necessary to obtain the entire I-E curve within the recorder scale. A typical I-E curve for the Pt disk electrode of a RRDE is shown in Figure 11. If the curve obtained differs substantially from that in Figure 11, refer to the section on troubleshooting in Chapter 4.

- The procedures in step 9 may be repeated for the ring electrode of a RRDE. Set the AUTO switch of the Model 366A to the ZERO position and transfer the lead from the disk electrode contact to the ring electrode contact. The area of the ring electrode on a RRDE is usually less than the area of the disk electrode, and the sensitivity of the Y axis may be increased to enlarge the I-E curve for the ring electrode. A typical I-E curve for the ring electrode of a RRDE is also shown in Figure 11.

3.3. EXPERIMENT B: MASS TRANSPORT-LIMITED CURRENTS AT THE ROTATING DISK ELECTRODE

The mass transport-limited faradaic current in the disk electrode of the RRDE, $I_{l,d}$, is a linear function of the square root of rotational velocity, $\omega^{1/2}$, as described by Equation 17. In this experiment, the square root dependence will be tested for the oxidation of I⁻ in 0.5 M H₂SO₄. The diffusion coefficient of I⁻ will be calculated from the slope of a plot of $I_{l,d}$ versus $\omega^{1/2}$.

- Repeat steps 1-3 of Experiment A substituting a solution of 0.5 M H₂SO₄ + 0.5 mM KI for the 0.5 M H₂SO₄ used in Experiment A.
- Set the controls of the Model 366A Bi-Potentiostat as indicated below.

<u>Section</u>	<u>Control</u>	<u>Position</u>
---	AC POWER	OFF
---	ELECTRODES	NORMAL
---		MODE POT
SWEEP GENERATOR	MANUAL	Center position (off)
SWEEP GENERATOR	AUTO	ZERO
SWEEP GENERATOR	SWEEP RATE	33.3 mV per sec
SWEEP GENERATOR	UPPER	+1.00 V
SWEEP GENERATOR	LOWER	+0.00 V
SWEEP GENERATOR	STOP AT LIMIT	Center position (off)
K1 ELECTRODE	OFFSET VOLTAGE	Center position (off)
K1 ELECTRODE	SWEEP VOLTAGE	ON
K1 ELECTRODE	CURRENT CONVERTER	0.5 mA per volt
K2 ELECTRODE	OFFSET VOLTAGE	Center position (off)
K2 ELECTRODE	SWEEP VOLTAGE	OFF
K2 ELECTRODE	CURRENT CONVERTER	20 mA per volt

- Repeat steps 5-8 from Experiment A for a rotation speed of 6400 rev/min.

- Place the MANUAL switch of the Model 366A momentarily in the UP position and place the AUTO switch in the ON position. The scan of the electrode potential will commence from 0.00 V, in the positive direction, and scan between the limits of +1.00 V and 0.00 V. Allow the electrode potential to cycle several times until the I-E curve is reproducible. Adjust the zero position of the Y-axis (current) so the entire anodic wave is contained on the scale of the chart paper. Record the I-E curve for the positive potential sweep. The anodic wave for oxidation of I^- will be clearly apparent. The sharp increase in anodic current at +0.90 V versus SCE corresponds to oxidation of I^- to IO_3^- .

Due to the presence of surface controlled reactions during the negative potential sweep, the anodic wave for the negative sweep is quite different from the wave for the positive sweep. A discussion of the surface-controlled reactions for a Pt electrode in an acidic solution of I^- is given by D. C. Johnson, *J. Electrochemical Soc.*, 119, 331 (1972).

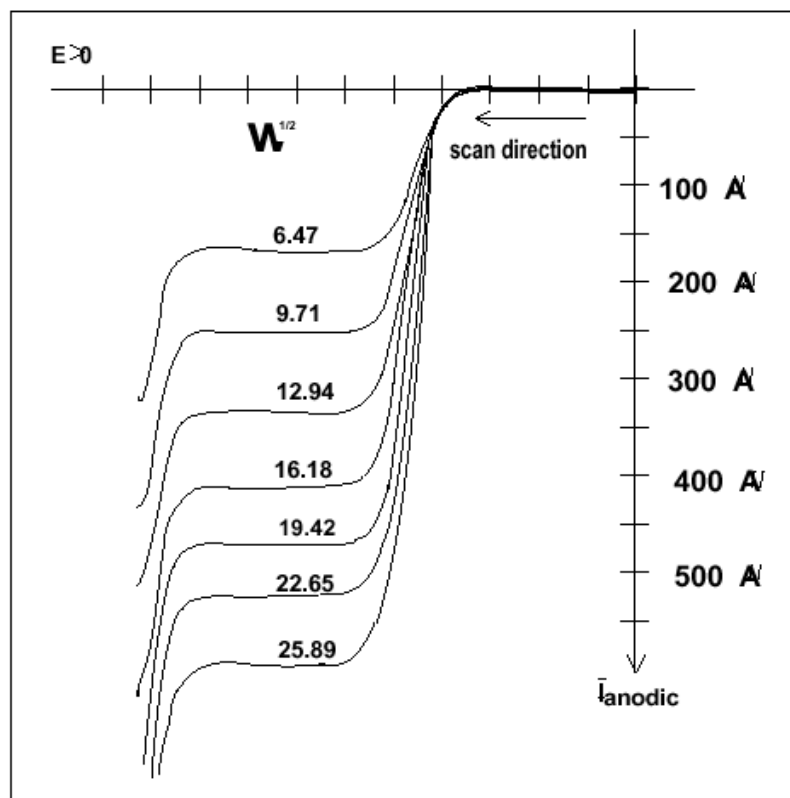
- Record the anodic wave during the positive potential sweep from 0.00 V to 1.00 V for the rotation speeds given below. The corresponding angular velocity and square root of angular velocity are also given.

Rotation Speed (rev/min)	ω (rad/sec)	$\omega^{1/2}$ (rad ^{1/2} /sec ^{1/2})
6400	670.2	25.89
4900	513.1	22.65
3600	377.0	19.42
2500	261.8	16.18
1600	167.6	12.94
900	94.2	9.71
400	41.9	6.47

Representative data for the disk electrode of an RRDE are shown in Figure 12.

- Plot values of limiting current at 0.750 V versus SCE for the disk electrode as a function of $\omega^{1/2}$. The plot is predicted to be linear. The intercepts of the plots will equal the charging current which passes in the electrode as a consequence of the potential scan. The charging current is independent of rotation speed, and the slope of the $I_l - \omega^{1/2}$ plot should be independent of the rate of potential scan.
- Calculate the diffusion coefficient for I^- from the slope of the $I_{l,d} - \omega^{1/2}$ plot according to Equation 17. The slope is given by Equation 31.

$$dI_{l,d}/d\omega^{1/2} = 0.62nFAD^{2/3}V^{-1/6}C_I^b \quad (31)$$



Recorder: X-axis sensitivity = 100 mV/cm
 Y-axis sensitivity = 100 mV/cm
 ZERO position indicated by +

Potential sweep: rate = 33.3 mV/sec
 range = +0.00 V to +1.00 V vs. SCE (curve recorded only during positive potential sweep)

Current sensitivity: disk = 0.5 mA/V (50 μ A/cm)

RRDE speeds = 400, 900, 1600, 2500, 3600, 4900 and 6400 rev/min

Solution: 0.5 M H₂SO₄ + 0.4897 mM KI

Figure 12. CURRENT-POTENTIAL CURVES FOR IODIDE AT A ROTATING PLATINUM DISK ELECTRODE

where

$$n = 1 \text{ equiv/mol}$$

$$F = 9.65 \times 10^4 \text{ coul/equiv}$$

$$A = \pi R_1^2$$

$$\nu^{-1/6} = 2.13 \text{ cm}^2/\text{sec for } 0.5 \text{ M H}_2\text{SO}_4$$

$$C_i^b = \text{concentration of } I^- \text{ (mol/liter)}$$

$$dI_{i,d}/d\omega^{1/2} = \text{slope (mA/rad}^{1/2}\text{sec}^{-1/2})$$

An example calculation of D is given below for the data in Figure 12.

$\omega^{1/2}$ (rad ^{1/2} /sec ^{1/2})	$I_{l,d}$ (μ A)
6.47	115
9.71	174
12.94	231
16.18	289
19.42	349
22.65	404
25.89	462

Least squares analysis:

$$y = mx + b$$

$$m = 17.866 \text{ (slope)}$$

$$b = +0.067 \text{ (intercept)}$$

$$r^2 = 0.9999 \text{ (correlation coefficient)}$$

$$17.866 = 0.6205 nFA_d D^{2/3} \nu^{-1/6} C_L^b$$

$$n = 1 \text{ eq/mol}$$

$$A_d = \pi R_1^2 = 0.459 \text{ cm}^2$$

$$\nu^{-1/6} = 2.13 \text{ cm}^2/\text{sec}$$

$$C_L^b = 0.4897 \text{ mM}$$

Calculation:

$$D^{2/3} = 17.866/28636.8 = 6.24 \times 10^{-4}$$

$$D = 1.56 \times 10^{-5} \text{ cm}^2/\text{sec}$$

3.4. EXPERIMENT C: COLLECTION AND SHIELDING EFFICIENCY OF A ROTATING RING-DISK ELECTRODE

In this experiment the theoretical and experimental values of the collection efficiency and shielding will be compared for a RRDE.

1. Repeat steps 1-8 of Experiment A as amended in steps 1-3 of Experiment B. If Experiment C is performed immediately after Experiment B, there is no need to replace the solution in the electrolysis cell and one can forego the lengthy deaeration process.

- Record the I-E curves during the positive potential sweep at the disk electrode and the ring electrode for a rotation speed of 1600 rev/min. These curves are obtained by procedures given in step 4 of Experiment B.

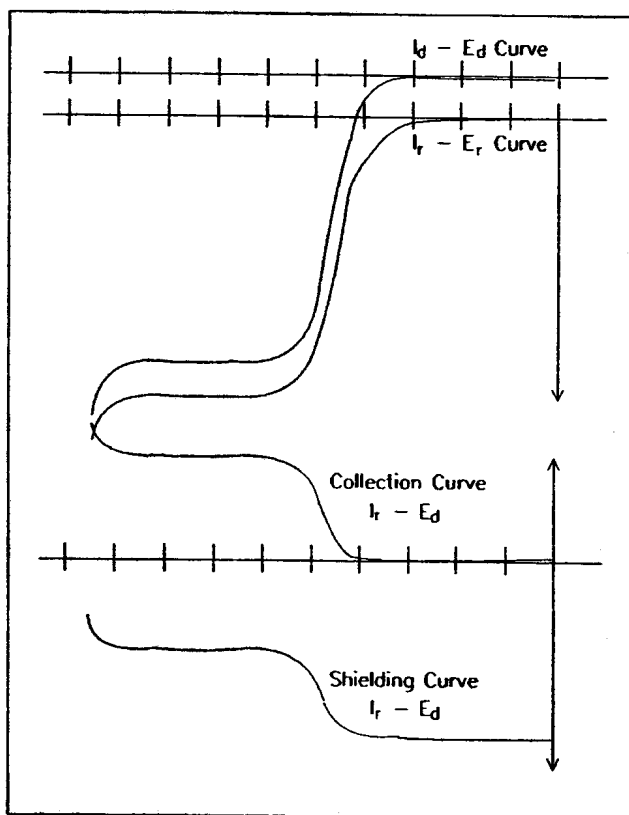
The I-E curve for the ring electrode is obtained exactly as for the disk electrode except the lead from the K1 jack on the SWEEP GENERATOR is connected to the contact for the ring electrode.

- Prepare the Model 366A for simultaneous potentiostatic control of the ring and disk electrodes.

Section	Control	Position
SWEEP GENERATOR	MANUAL	Center position (off)
SWEEP GENERATOR	AUTO	ZERO
SWEEP GENERATOR	SWEEP RATE	33.3 mV per sec
SWEEP GENERATOR	UPPER	+1.00 V
SWEEP GENERATOR	LOWER	+0.00 V
SWEEP GENERATOR	STOP AT LIMIT	Center position (off)
K1 ELECTRODE	OFFSET VOLTAGE	Center position (off)
K1 ELECTRODE	SWEEP VOLTAGE	OFF
K1 ELECTRODE	CURRENT CONVERTER	0.5 mA per volt
K2 ELECTRODE	OFFSET VOLTAGE	Center position (off)
K2 ELECTRODE	SWEEP VOLTAGE	OFF
K2 ELECTRODE	CURRENT CONVERTER	0.2 mA per volt

Make electrical connection from the jack for K1 on the SWEEP GENERATOR section to the disk electrode contact on the RRDE. Similarly connect the jack for K2 to the contact for the ring electrode. Both the ring and disk electrodes are now potentiostated at 0.00 V versus SCE. Transfer the leads connected to the Y-axis input of the recorder from the I1 jacks to the I2 jacks of the Model 366A. The Y-axis is now ready to record the ring electrode current.

- The ring electrode is at a potential of 0.00 V versus SCE which is suitable for mass transport-limited reduction of I_2 . Record the ring current as a function of disk potential ($I_r - E_d$) during the positive sweep of disk potential from 0.00 V to 1.00 V versus SCE for a rotation speed of 1600 rev/min. The $I_r - E_d$ curve for $E_r = 0.00$ V is known as the *collection curve*. A typical collection curve is shown in Figure 13.
- Adjust the potentiometer of the OFFSET VOLTAGE for K2 ELECTRODE (ring electrode) to a setting of 2.75 which corresponds to a potential of 0.750 V (3.75×0.2 V/turn). Set the OFFSET VOLTAGE switch to the + position. The ring electrode potential is now at 0.750 V versus SCE for which the oxidation of I^- occurs at a rate limited by mass transport. Record the $I_r - E_d$ curve for the positive sweep of the disk potential from 0.00 V to 1.00 V versus SCE at a rotation speed of 1600 rev/min. The $I_r - E_d$ curve for $E_r = 0.750$ V is known as the *shielding curve*. A typical shielding curve is shown in Figure 13.



Recorder: X-axis sensitivity = 100 mV/cm
 Y-axis sensitivity = 100 mV/cm
 ZERO position indicated by +

Potential sweep:
 rate = 33.3 mV/sec
 range = +0.00 V to +1.00 V vs. SCE (curves recorded only during positive potential sweep)

Current sensitivity:
 $I_d - E_d$ curve = 0.5 mA/V (50 μ A/cm)
 $I_r - E_r$ curve = 0.2 mA/V (20 μ A/cm)
 shielding curve = 0.2 mA/V (20 μ A/cm)
 collection curve = 0.2 mA/V (20 μ A/cm)

RRDE Speed = 1600 rev/min

Solution: 0.5 M H₂SO₄ + 0.4897 mM KI

Figure 13. I-E CURVES FOR IODIDE AT A PLATINUM RING-DISK ELECTRODE.

- When experimentation is completed, shut down the instrumentation by switching off the AC POWER to the recorder and then the Model 366A. Remove the solution from the electrolysis cell and clean all glass surfaces by thorough rinsing with distilled water. Be certain to drain and rinse the Luggin capillary so the contents will not be a source of contamination in later experiments. The fritted glass of the gas dispersion tube and the counter electrode compartment should be flushed several times with distilled water to remove all traces of acid and KI. Store all glassware in a clean environment. Remove the electrode and carefully rinse it with distilled water. Store the electrode in a clean place.

7. Calculate $\beta^{2/3}$, the shielding coefficient, S, and the collection efficiency, N_0 , from the current-potential curves obtained in this experiment. Refer to Equations 24-26 and Figure 13 for assistance.
8. Determine the characteristic radii of the RRDE using an optical micrometer. Calculate the collection efficiency for the RRDE. Also, calculate the shielding efficiency. Compare the experimental and theoretical values of $\beta^{2/3}$, N_0 and S. The values should agree within 10% relative error.

Example calculations of $\beta^{2/3}$, N_0 and S are given below for the data in Figure 13.

RRDE dimensions:

$$\begin{aligned} R_1 &= 0.3822 \text{ cm} \\ R_2 &= 0.4010 \text{ cm} \\ R_3 &= 0.4255 \text{ cm} \end{aligned}$$

Area of disk electrode:

$$A_d = R_1^2 = 0.459 \text{ cm}^2$$

Theoretical $\beta^{2/3}$:

$$\beta^{2/3} = [(R_3/R_1)^3 - (R_2/R_1)^3]^{2/3} = 0.370$$

Collection efficiency predicted (from Table 2):

$$R_2/R_1 = 1.049$$

$$R_3/R_1 = 1.061$$

$$N_0 = 0.179 \text{ (17.9\%)}$$

Shielding efficiency predicted:

$$S = 1 - N_0/\beta^{2/3} = 0.515 \text{ (51.5\%)}$$

Experimental results:

$$I_{i,d}(E_d = 0.750 \text{ V}) = 236 \mu\text{A}$$

$$I_{i,r}(E_r = 0.750 \text{ V}) = 89.5 \mu\text{A}$$

$$I_r(E_d = 0.0 \text{ V}; E_r = 0.0 \text{ V}) = 0.0 \mu\text{A}$$

$$I_r(E_d = 0.750 \text{ V}; E_r = 0.0 \text{ V}) = 44.5 \mu\text{A}$$

$$I_r(E_d = 0.000 \text{ V}; E_r = +0.750 \text{ V}) = 89.0 \mu\text{A}$$

$$I_r(E_d = 0.750 \text{ V}; E_r = 0.750 \text{ V}) = 44.0 \mu\text{A}$$

$$\beta^{2/3} = 89.5 \mu\text{A}/236 \mu\text{A} = 0.379 \text{ (0.370 theoretical)}$$

$$N_0 = 44.5 \mu\text{A}/236 \mu\text{A} = 0.189 \text{ (0.179 theoretical)}$$

$$S = (89.0 - 44.0 \mu\text{A})/89.0 \mu\text{A} = 0.506 \text{ (0.515 theoretical)}$$

4. PRELIMINARY TESTING

4.1. INTRODUCTION

When a malfunction or some anomalous behavior is observed during electrochemical experiments, one must first determine whether the difficulty originates within the bi-potentiostat or is external to it. To facilitate troubleshooting, a so-called dummy cell has been provided in the bi-potentiostat. The dummy cell is constructed from four resistors with a common connection as shown in Figure 14. When the function switch labeled ELECTRODES at the left side of the front panel on the Model 366A is in the dummy position, all connections to the electrolysis cell are disconnected and internal connections of CE, K1, K2 and REF are made to the dummy cell as shown in Figure 14. In effect, simple resistance analogs are substituted for the functions of the normal electrodes in the electrolysis cell.

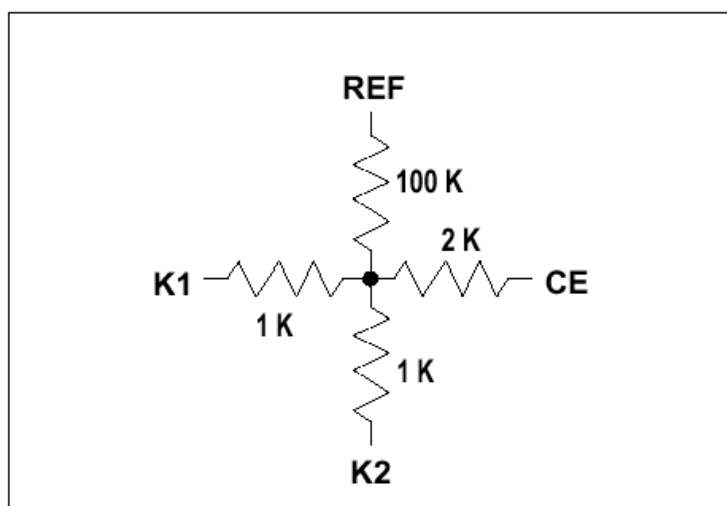


Fig. 14. DUMMY CELL.

Starting with the controls of the Model 366A and the X-Y recorder set as described in Experiment A, steps 5 and 6, change the ELECTRODES switch from normal to dummy. Change the CURRENT CONVERTER switch on the K1 ELECTRODE section from 0.2 mA/V to 2 mA/V. Turn on the AC POWER switches for the Model 366A, the X-Y recorder and the digital voltmeter (if needed). The recorder pen should be at the ZERO position on both axes and the voltmeter should read 0.00 ± 0.01 V. Start the potential scan in the positive direction as in Experiment A, step 11. The recorder should display a straight line of slope +1/2. If the recorder does not display a straight line of slope +1/2, check the leads from the Model 366A to the recorder; also check all control settings.

Many electrochemical experiments with ring-disk electrodes proceed with potentiostatic control of the ring electrode at a constant potential while the potential of the disk electrode is scanned within certain prescribed limits.

Check that the SWEEP VOLTAGE switch for K1 ELECTRODE (disk) is ON and the SWEEP VOLTAGE switch for K2 ELECTRODE (ring) is OFF. Set OFFSET VOLTAGE of K2 ELECTRODE to 0.10 V. The output at the E2 jack should read 0.10 V through the potential scan of the K1 electrode.

Successful completion of these tests indicates that the Model 366A Bi-Potentiostat is operating correctly, and that the bi-potentiostat and recorder are properly interconnected. The cause of the malfunction is thus located external to the bi-potentiostat in the connections to the electrolysis cell or within the cell itself. A troubleshooting guide is provided below to assist in localizing several commonly encountered problems related to the electrolysis cell.

Failure of these tests indicates a malfunction of the Model 366A or the X-Y recorder. Consult Princeton Applied Research for assistance with electronic problems in the Model 366A Bi-Potentiostat.

4.2. TROUBLESHOOTING

The troubleshooting guide below will help localize problems that are commonly encountered in the use of rotating disk and ring-disk electrodes. It is assumed that the dummy cell test described above has been successfully completed.

Problem/Possible Explanation

1. No K1 current recorded over entire potential scan, i.e., Y-axis of recorder remains at ZERO; X-axis scans normally.

Discontinuity in K1 circuit. Examples: electrode not contacting solution; electrode surface covered with gas bubble; break in lead between K1 jack on Model 366A and electrode contact on rotator; discontinuity in contact.

Suggestion: Check discontinuities in lead and contact with ohmmeter.

2. Y-axis of recorder is off scale over entire scan, i.e., potentiostat output is saturated.

Reference or counter electrodes not connected to potentiostat. Examples: chambers for counter electrode and/or reference electrode not filled with electrolyte solution; Luggin capillary not filled with electrolyte solution; bubble in Luggin capillary; ground-glass stopcock of Luggin capillary not wetted with electrolyte solution; defective reference electrode.

Problem/Possible Explanation

Suggestions: Check filling solution of reference electrode. A crystal in the tip of the reference electrode can terminate ionic continuity; replace reference electrode as a temporary test.

3. Electrical noise observed on Y-axis of residual current-potential curve, Experiment A, in region of adsorbed hydrogen (0.0 V to -0.2 V vs. SCE).

Dirty electrical contacts on rotator.

Suggestion: Gently clean contacting surfaces with abrasive paper.

Bubbles impinging on electrode surface during potential scan.

Suggestion: N₂ should not be dispersed into electrolyte solution during electrochemical experiments.

Intermittent discontinuity in leads from Model 366A to electrolysis cell.

Suggestion: Wiggle each lead to determine source.

System not grounded or ground loops exist between bi-potentiostat and recorder (and voltmeter if used).

Pickup of electrostatic noise by reference electrode.

Suggestion: When operating the bi-potentiostat at a very high current sensitivity, it may be necessary to place a grounded shield constructed from copper screen around the reference electrode to minimize the pickup of electrostatic noise.

4. Current at $E = 0.3$ V vs. SCE on residual current-potential curve is larger than normal for properly functioning electrode of comparable area at same rotation speed (See Figure 15).

Dissolved O_2 remains in solution.

Suggestion: Continue deaeration for 10-15 minutes.

If proper character of I-E curve is not obtained in the region of $E = 0.3$ V, proceed as follows:

Problem/Possible Explanation

- a. Increase rate of N_2 flow;
- b. Improve cell lid to decrease chance of dissolution of air from room atmosphere.

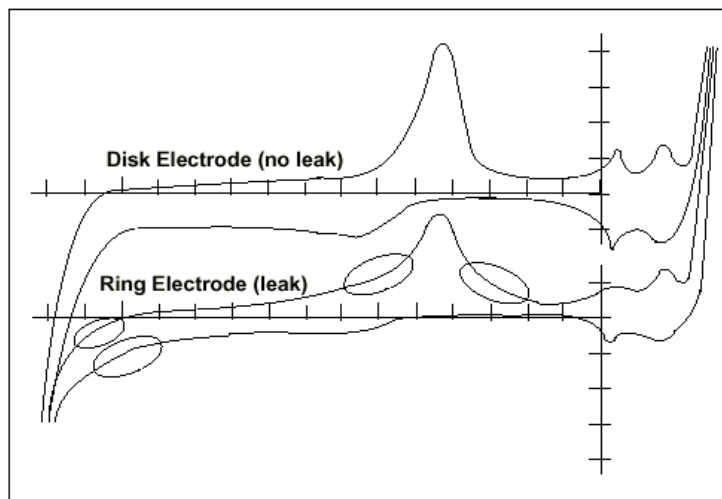
Suggestion: Use of an unnecessarily long piece of plastic tubing to connect the N_2 tank and the gas dispersion tube of the cell is not advised because of the permeability of plastic by oxygen.

In the absence of dissolved O_2 , the residual current observed at $E = 0.3$ V vs. SCE on the positive potential sweep is approximately equal in magnitude, but opposite in polarity, to the current for the negative potential sweep (see Figure 11).

5. Current at $E = 0.7$ V vs. SCE on residual current-potential curve is larger than normal. See I-E curve in Figure 15 for ring electrode that has developed a capillary leak.

Probability that the seal surrounding the electrode has developed a capillary leak.

Suggestion: Replace electrolyte solution with fresh solution to be certain that electroactive impurities are not present in the cell.



(All parameters as in Figure 11. Anomalous regions indicating leak are circled on $I_r - E_r$ curve.)

Figure 15. CURRENT-POTENTIAL CURVES FOR NORMAL DISK ELECTRODE AND LEAKY RING ELECTRODE.

INDEX

Amplifier specifications	7	MANUAL	6
AUTO switch	6	MODE	6
Circuit description	10	STOP AT LIMIT	6
Compliance voltage	5	SWEEP VOLTAGE	8
Corrosion research	1	Titration, diffusion layer	5, 23, 24
CURRENT CONVERTER switch	6	UPPER controls	6
Dummy cell resistors	7, 37		
ELECTRODES switch	6		
Fuse rating	4		
Fuse replacement	4		
Galvanostatic operation	6		
Grounding	9		
Jacks			
CE	8		
E1	8		
E2	8		
ELECTRODE	8, 9		
GAL	8		
ground	5		
I1	6, 8		
I1-I2	8		
I2	6, 8		
IN	8		
K1	8, 10		
K2	8, 10		
REF	8, 9		
SWEEP VOLTAGE	8		
Leaky electrodes	39		
Line voltage	3		
LOWER controls	6		
MANUAL switch	6		
MODE switch	6		
Noise	5		
OFFSET VOLTAGE controls	6		
Potentiostat mode	1		
Power cord	3		
Power line voltage	3		
Reaction mechanisms	1		
Ring-disk electrode	35		
Rise time of amplifiers	5		
Rotating disk electrode	14		
Rotating ring-disk electrode	25, 34, 35		
Safety considerations	2		
Service	4		
Shielding, grounded	39		
Shipping damage	2		
STOP AT LIMIT switch	6		
Surface-controlled reactions	30		
Switches			
AUTO	6		
CURRENT CONVERTER	6, 8		
ELECTRODES	6		

