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**ANALYSIS OF MINI-POTENTIOSTAT DESIGN
OPTIONS FOR CORROSION RESEARCH**

BY H. A. NEWBORN D. C. BRATLIE
RESEARCH AND TECHNOLOGY DEPARTMENT

1 SEPTEMBER 1978

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SUMMARY

This document reports the results of an analysis of various electronic design configurations for a mini-potentiostat to be used in corrosion research. A candidate circuit design is described and its operation is compared with that of other units.

The work is being supported by the Naval Air Systems Command and by NSWC Independent Research funds.

The work is being reviewed by Dr. C. Robert Crowe, Metallic Materials Branch.

J. R. Dixon
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PREFACE

This interim report describes an analysis of mini-potentiostat design configurations. A particular model, utilizing modern operational amplifier components, was found to be economical while performing adequately under simulated corrosion experiments.

The authors wish to acknowledge Mr. Donald Brickerd for his aid in constructing the model DH Potentiostat, and to Dr. C. Robert Crowe and to Mr. Hampton DeJarnette for their constructive comments in discussions.

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INTRODUCTION

The goal of the present research was to design a mini-potentiostat suitable for corrosion studies. Specific experimental requirements were to be met using a device built from state-of-the-art components which would be economical and show long term electronic stability.

For more than thirty-five years, electronic devices, now known as potentiostats, have been utilized in controlled studies of electrochemical phenomena. A potentiostat is designed to maintain a precisely controlled potential across electrochemical cell electrodes. Since the applied voltage is different from that found at steady state between the dissimilar electrodes in a given medium, a current flow is impressed upon the system. In a corrosion study, for example, a material to be studied can be made more anodic than is natural and a controlled corrosion rate can be maintained. The importance of precise voltage regulation is apparent as the electrode potential is directly related to the thermodynamic ΔG (change in Gibbs free energy) associated with the electrochemical reaction to be studied. This must remain constant throughout the experimentation for obtaining meaningful data. In a similar fashion, a material to be studied can be made more cathodic and, thus, current is forced into it, providing protection from the corrosive environs. An excellent review of the functions of a potentiostat is given by Gileadi.

The dynamic and electrically sensitive nature of an electrochemical cell requires that the addition of an electronic control circuit must not disturb the ongoing chemical phenomena. As a result, a third electrode, electrically isolated from the working cell is used as the standard reference voltage. It is the voltage difference between the reference electrode and the working electrode which is to be controlled. A control range of -6 volts to +6 volts is regarded as sufficient for most corrosion experiments. The second electrode in what has been called the working cell, denoted the counter or auxiliary electrode, acts as a source or sink of current required to maintain the set potential between working and reference.

The reference electrode could be "polarized" by external currents inadvertently introduced into the system (on the order of nanoamperes). Therefore, a device with very high input impedance ($>10^{10}$ ohms) is required. At the onset of phenomena such as pitting or crevice corrosion, large changes in electrochemical potential are known to occur. It is important, therefore, that the potentiostat maintain its voltage control over a wide range of both steady and transient conditions. This translates, electronically, into the ability of the device to function over many orders of magnitude of output current flowing between the working and counter electrodes. Ultimately, the limitations of the potentiostat in current capacity will limit the size of the test specimen (larger specimen area, larger current).

Ideally, operational amplifiers (op-amps) should provide a convenient mechanism for the voltage control required. A good review of the fundamental work on simplified design types utilizing early op-amps is given by Schroeder.² It was shown³ that among the many basic configurations in which to arrange the necessary electronic components no simplified circuit would meet all the requirements of a potentiostat. The work of the present, then, becomes an optimization for specific experimental requirements using state-of-the-art electronic components.

Since no simple circuits can perform the total range of electrochemical experiments adequately, and since the market for such instrumentation is limited, multipurpose expensive commercial units using complex circuitry have become the norm for a corrosion laboratory. The added expense becomes a problem when there is a need to perform long term or multi-specimen experiments.

This paper discusses a mini-potentiostat design which will provide an alternative.

1. Gileadi, E. et al, Interfacial Electrochemistry (Addison-Wesley, 1975), pp. 151-205.
2. Schroeder, R. R., "Operational Amplifier Instruments for Electrochemistry," Computers in Chemistry and Instrumentation Vol. 2, Ch. 10 (Marcel Dekker, Inc., 1972), pp. 263-350.
3. Schwarz, W. M. and Shain, I., Analytical Chemistry, Vol. 35, 1963, p. 1770.

POTENTIOSTAT DESIGN (DH MODEL)

The ultimate specification to be met by the mini-potentiostat was defined as its capability to maintain an error in set potential (i.e. the difference between a dialed-in desired potential between working and reference and that actually measured) of less than one millivolt while handling output currents of up to one ampere. Therefore, the primary experiment performed for the evaluation of design options was a check of the voltage regulation between v_o (that which was set) and v_L (that which was measured across a variable resistive load used as a cell analog). [$\Delta v \equiv v_o - v_L$; $i \equiv$ output current]

The DH Potentiostat, shown schematically in Figure 1, consists of several subsections. The operational amplifiers incorporated in the circuit perform three distinct functions. They serve as a voltage follower, a summer, and as a current to voltage converter.

Operational amplifier U1, and its associated components, are used to convert the current flowing through the working electrode to a voltage, which is read from a voltmeter. This amplifier must be capable of sinking up to one ampere of current, per the specifications cited earlier. The LH0021CK op-amp was chosen as its capacity is larger than that of more conventional op-amps and its price is not prohibitive. Other, more expensive components are available, and might be utilized to adapt the current design for higher current output experiments. The resistor network connected to the non-inverting input is used to cancel the input offset voltage to obtain accurate current readings. The two 0.5Ω resistors act as current limiters to protect the operational amplifier from shorts on the output. The feedback resistor a 1Ω 1% component, enables the current to be read on any voltmeter as:

$$v_{out} = r_f i_{in}$$

The voltage followers provide a very high input impedance ($>10^{10}$ ohms) to minimize loading. National Semiconductor LM310 devices perform this function. U3 is used to eliminate loading of the reference electrode. U2 isolates the set potentiometer from the summer. These two voltage followers are required for isolation of one part of the circuit from the rest of the circuitry to help attain good performance.

The CA3160 amplifier is used to sum the voltage inputs to the potentiostat. The reference to working electrode potential is compared to the set voltage by summing. The op-amp changes the circuit conditions so that the respective magnitudes are exactly equal. An auxiliary input is provided for use with special voltage forms which the experimenter might wish to impress upon the working electrode. A potentiometer is provided to null out the offset voltage of the summer in combination with U5, the LH0021CK current booster (one potentiometer corrects two op-amp set points).

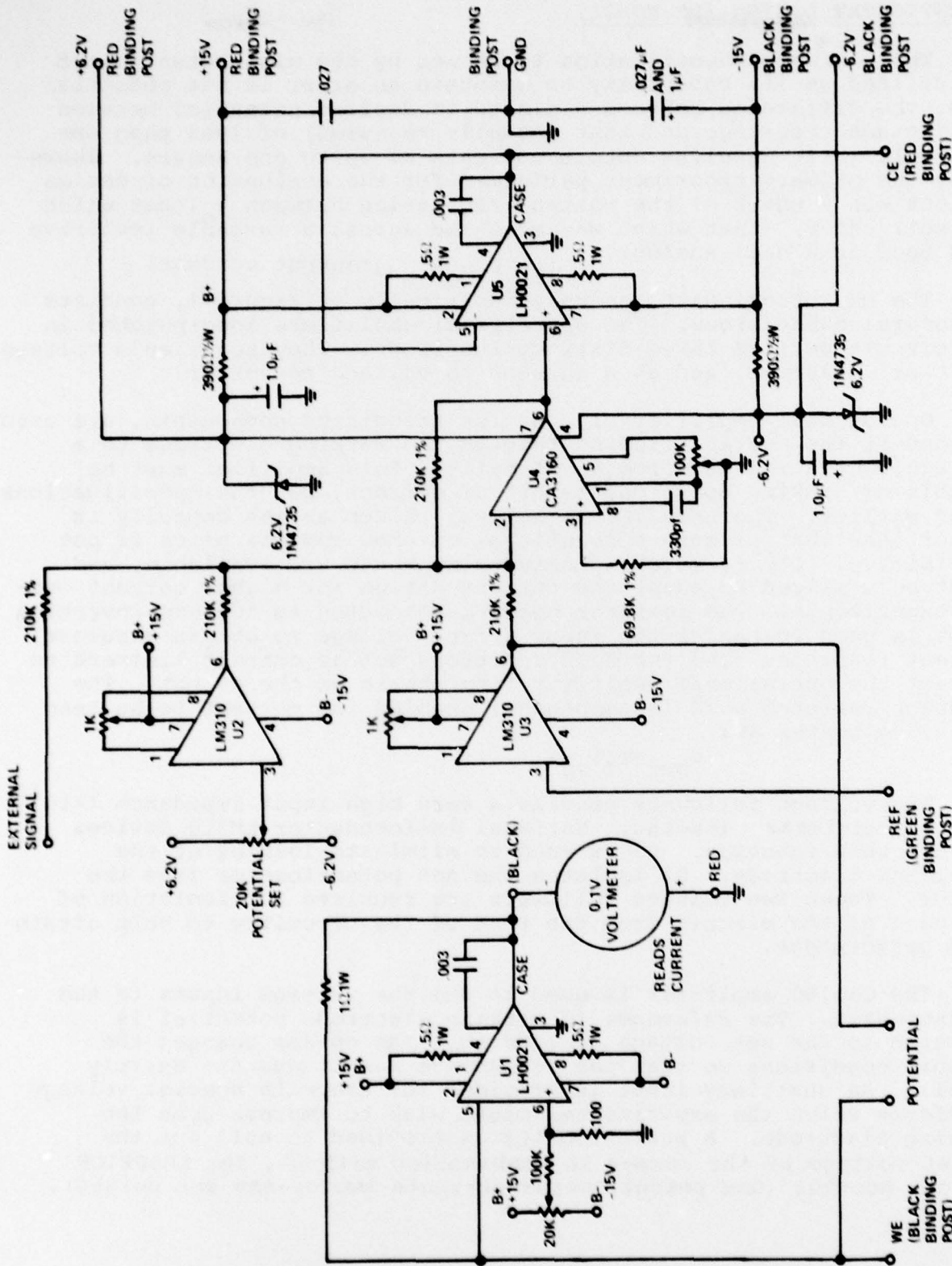


FIGURE 1 SCHEMATIC OF THE DH POTENTIOSTAT

The current booster circuit is used to drive large currents through the experimental cell. It is a high power operational amplifier (LH0021CK) connected as a voltage follower. This configuration sacrifices voltage gain for low output impedance and high input impedance. Low output impedance is very important in the previously discussed applications where excellent voltage regulation is required. The effective output impedance is divided by a factor of:

$$\left\{ \left(\frac{\text{open loop gain}}{\text{closed loop gain}} \right) + 1 \right\}$$

The closed loop gain equals unity in a voltage follower, so the output impedance is greatly reduced, minimizing output voltage changes with current fluctuations.

The first model of the DH Potentiostat was constructed in a 3" x 4" x 5" box with an attached heat sink to mount the power op-amps. A photograph of the assembled unit is included in the report as Figure 2. If the device is used at maximum current (one amp) and at a low set potential, the LH0021CK's must dissipate approximately 14 watts each. A large heat sink is, therefore, required. Numerous binding posts facilitate connection of the mini-potentiostat to the experimental apparatus. The power supply connections, meter outputs, electrode connections, auxiliary power outputs, and sweep input connections are available. An external sweep module can be constructed to plug into the external power and sweep binding posts.

The desired voltage input is set by turning the potential set knob until the required value is read on the meter connected to the "potential" binding posts. These posts are internally connected to the working electrode and the output of the voltage follower associated with the reference electrode.

An important concern is the stability of the potentiostat with time and temperature. Although no tests have yet been run on component aging, the specifications of the devices indicate drifts on the order of 10 microvolts per week. Presently there is some instability with continuous operation at high currents (> 500 ma). It is believed the difficulty arises because of the temperature rise of the LH0021CK operational amplifiers. If the high currents are momentary (< 1 sec) as expected in the experiments, there is no problem. If continuous operation at high current is required, the most obvious solutions are the use of a larger heat sink or a fan.

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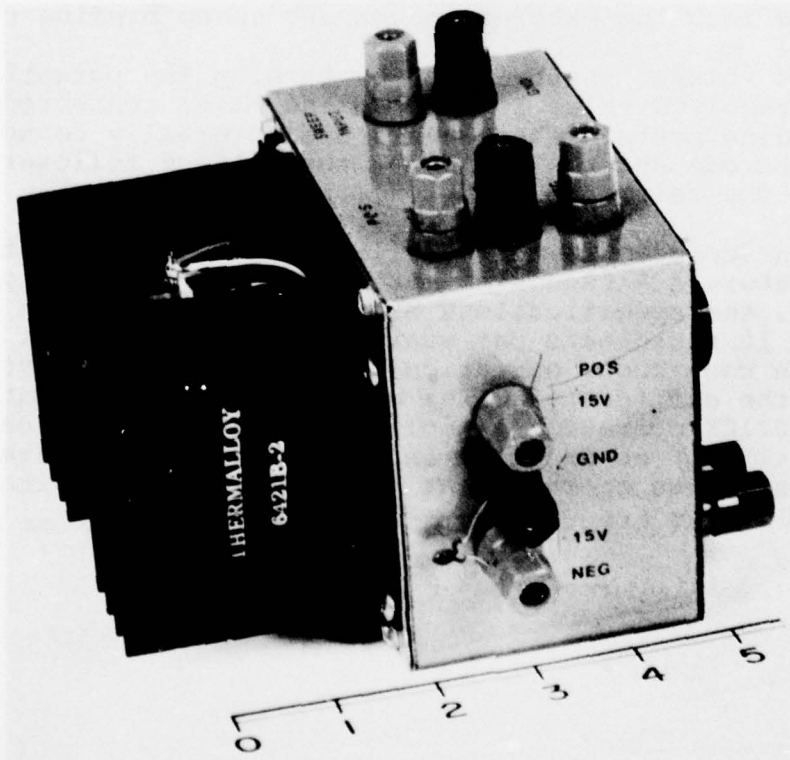
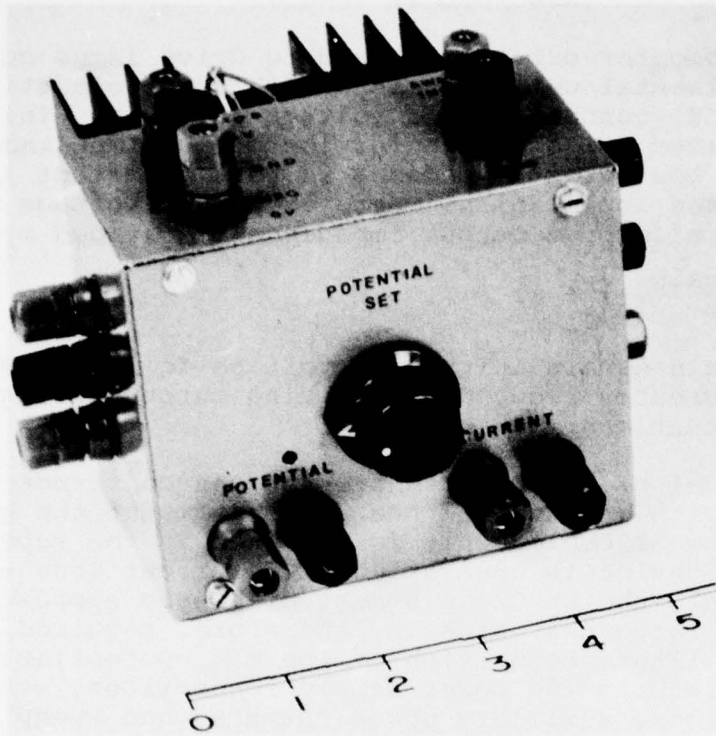


FIGURE 2 PHOTOGRAPHS OF A MODEL DH POTENTIOSTAT (FRONT, SIDE VIEWS)

DISCUSSION

The DH Potentiostat was compared with several other circuits for evaluation. The first design evaluated was a unit produced by Engelhard Industries known as a Capac Polaristat. The application of the unit, as described by the manufacturer, is "the study and application of automatically controlled impressed current cathodic protection." The unit was marketed in a metal cylinder, 6 inches long, 1 5/16 inch in diameter, adaptable to an auto battery as a power supply for the current required to provide cathodic protection. Since the components of the Polaristat were encased and since Engelhard had stopped producing the units, a schematic was obtained and a circuit of the same design was constructed. This schematic is shown in Figure 3.

The voltage regulation obtained using this design was extremely poor. It was suspected that since this unit was based on a differential amplifier, it was of great importance to match the field effect transistors which control the two legs of the differential to keep the voltages and currents balanced in each leg. Another drawback to this kind of design is that it is not adaptable for both anodic and cathodic control.

Since a fundamental principle underlying operational amplifier performance is their ability to hold voltages at the plus and minus inputs nearly equal, a few configurations were attempted using a single op-amp. The set voltage was entered at the plus input of the amplifier, while the minus input was associated with the potential across the load. Two of the variations attempted utilized high input impedance RCA type CA3160 operational amplifiers connected with high gain power transistors to the output for current boosting. These variations were designated "Darlington" and "Emitter Follower." Figure 4 is a schematic representation of these designs.

The voltage regulation of these units met the specification cited earlier for output current up to approximately forty milliamperes. This was a significant improvement over the differential amplifier and instilled hope for success.

The authors became aware of work being done by Mansfeld et al⁴ to design an inexpensive potentiostat. At about the same time, op-amps capable of sinking one ampere were ordered, with an eye toward meeting the specification cited earlier. It was hoped that high input impedance amplifiers could be found, but, none would deliver one ampere. Therefore, buffer stages utilizing National Semiconductor LM310 integrated circuits with high input impedance would be needed.

4. Mansfeld, F. and Inman, R. V., Proceedings NACE Corrosion/78 Houston, Paper Number 168.

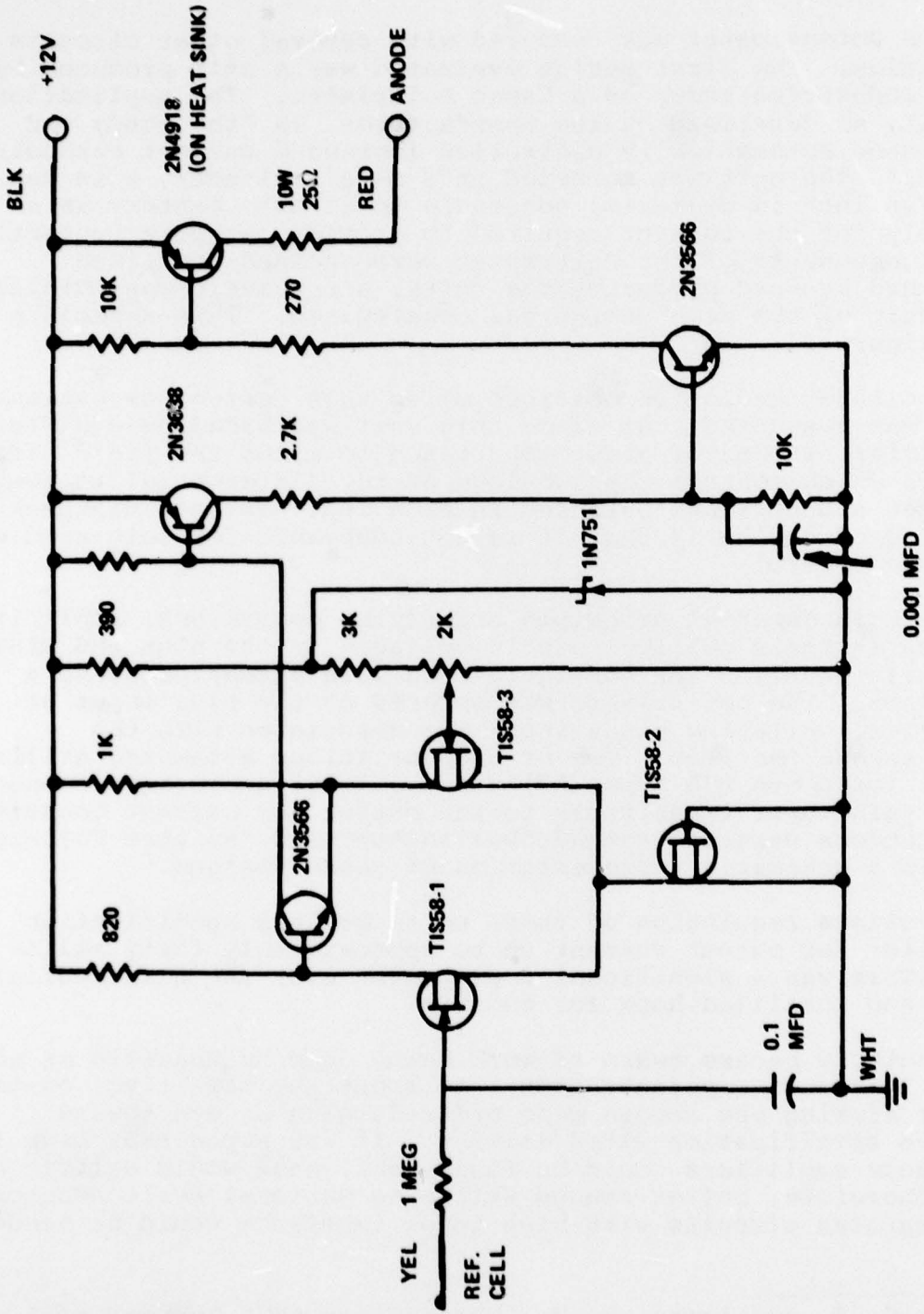
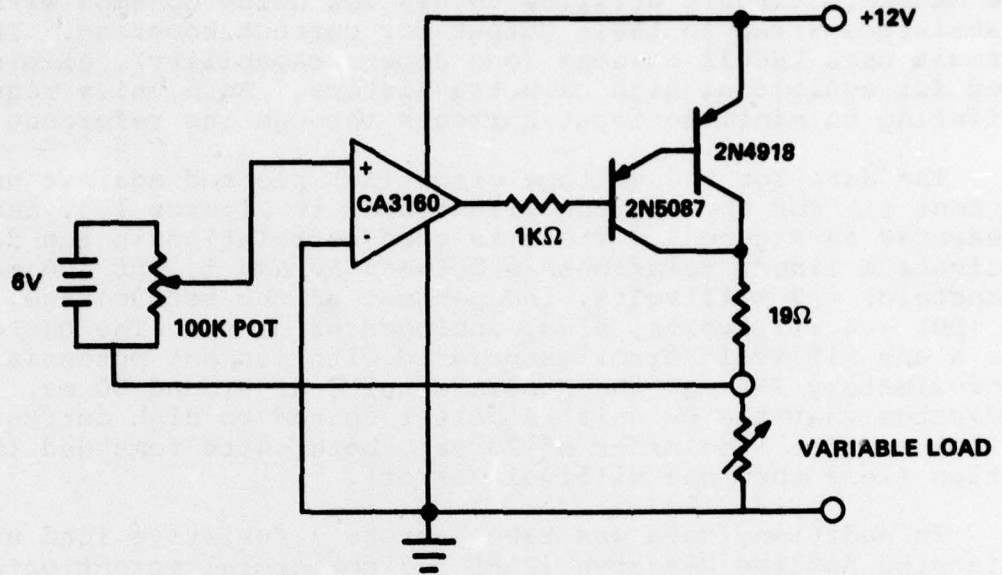


FIGURE 3 SCHEMATIC OF THE CAPAC POLARISTAT

"DARLINGTON"



"EMITTER FOLLOWER"

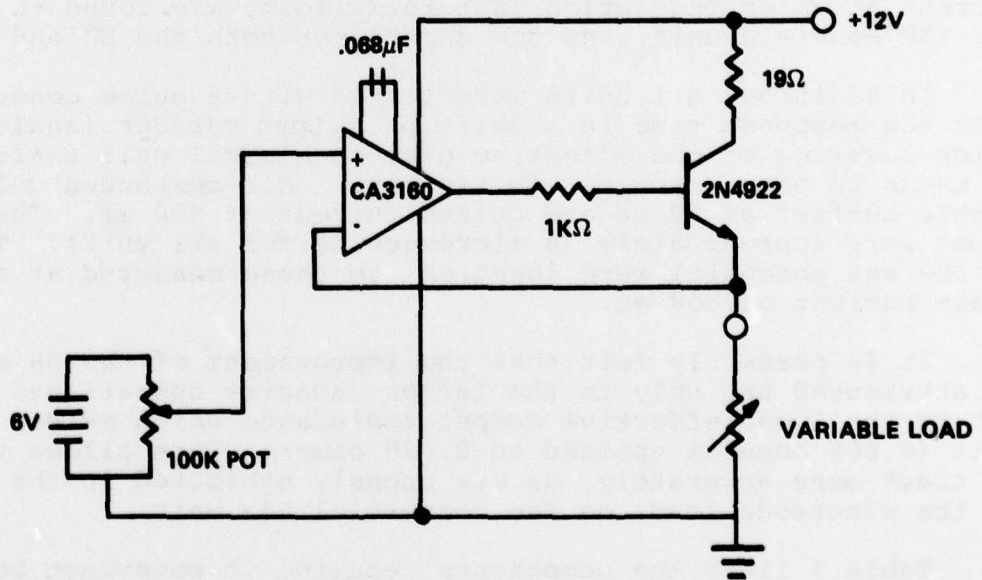


FIGURE 4 SCHEMATICS OF THE "DARLINGTON" AND "EMITTER FOLLOWER" OPTIONS

Figure 5 is a schematic diagram of the Mansfeld Potentiostat. The DH Potentiostat (developed at NSWC) was illustrated previously in Figure 1. Both units were built and tested with good results. The Mansfeld circuit utilizes LH0044 low noise op-amps with power transistors wired to their output for current boosting. The DH circuit uses LH0021 op-amps (one ampere capability), eliminating the need for additional high gain transistors. Both units require buffering to minimize input currents through the reference electrode.

The data for the voltage error (Δv) plotted against output current (i) for the options illustrated in Figures 1, 4, and 5 is presented in Figure 6. There is good correlation in the data to indicate a linear relationship between Δv and i . At 500 ma, Δv (Mansfeld) = 9 millivolts, independent of the set voltage, v_o , whereas Δv (DH) = 4 millivolts, also, independent of v_o . The DH Potentiostat has a one millivolt error associated with its Set potential at approximately 150 ma; the Mansfeld unit, at around 80 ma. The data indicates that the DH unit is better suited to high current operation. At low current (the order of 20 ma), both units remained in specification (less than one millivolt error).

In addition, data was taken across a resistive load using a Princeton Applied Research (PAR) 173 commercial potentiostat. Only after adapting the unit by shortening its standard leads was a 1 mv error specification obtained; as is, the unit performed comparably to the DH Potentiostat. The maximum output current, that is, the current at which regulation is totally lost, was found to be 600 ma, for the Mansfeld unit, and one ampere for both the DH and PAR units.

In addition, all units were tested with a pulse generator to test the response time in a shift of output current (analogous to a quick lowering of the effective electrochemical cell resistance, as is known to occur upon pit initiation). All responded well with the stable current at 50 ma and pulsed current of 500 ma. The response times were approximately 30 microseconds for all units. The errors in the set potential were identical to those measured at steady state current of 500 ma.

It is presently felt that the improvement of the DH model can be attributed not only to the larger capacity operational amplifiers, but to the lower effective output resistance which exists in the DH unit (0.009 ohms as opposed to 0.020 ohms). This allows the unit to track more accurately, as was grossly exhibited in the shortening of the electrode leads on the commercial PAR unit.

Table 1 lists the components required to construct both the Mansfeld and the DH Potentiostats. At the time of this report, the retail cost of the parts for each unit is similar.

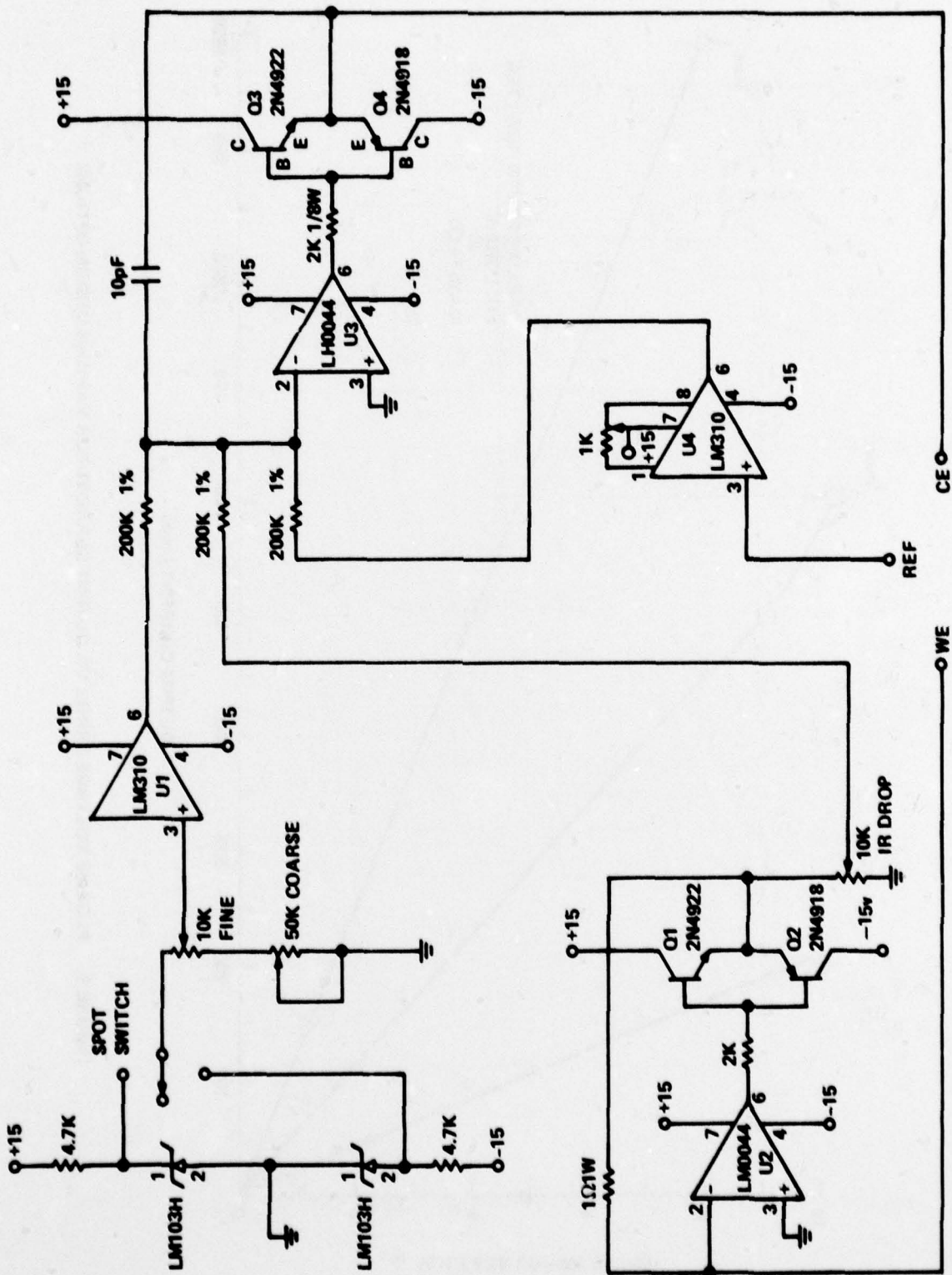


FIGURE 5 SCHEMATIC OF THE MANSFELD POTENTIOSTAT

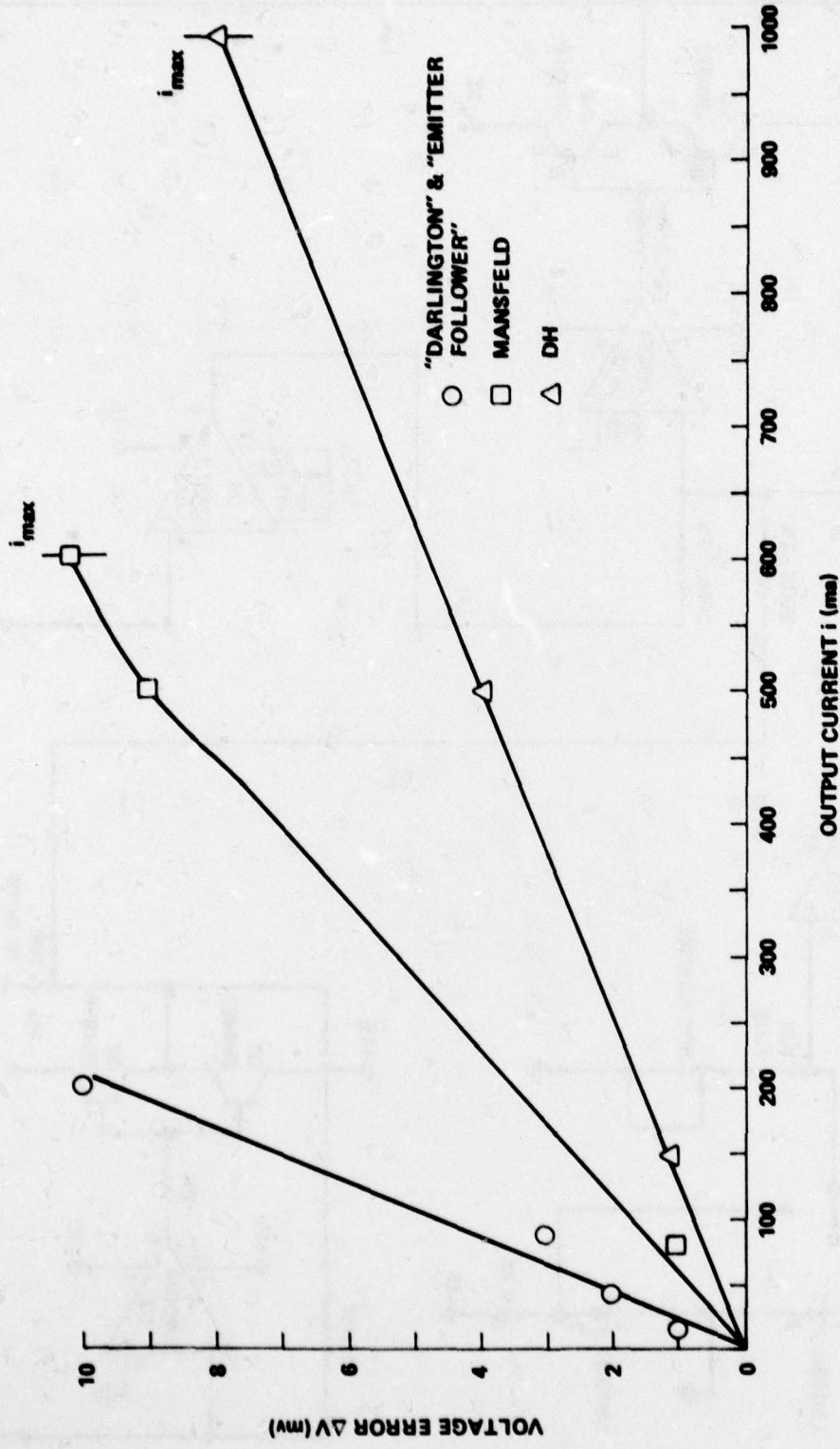


FIGURE 6 PLOT OF VOLTAGE ERROR VS. OUTPUT CURRENT FOR VARIOUS DESIGN OPTIONS

Table 1

PARTS LIST

MANSFELD			DH		
No.	Component	Retail Price	No.	Component	Retail Price
2	LH0044BH	\$36.90	2	LH0021CK	\$38.20
2	2N4922	1.70	2	LM310	5.20
2	2N4918	1.66	1	CA3160AE	3.25
2	LM310	5.20	2	1K Ω multiturn pot.	2.00
2	LM103H	14.40	1	100K Ω multiturn pot.	1.00
3	200K Ω 1% resistors	3.00	1	20K Ω multiturn pot.	1.00
2	10K Ω pot.	4.00	1	20K Ω 10 turn pot.	6.25
1	50K Ω pot.	2.00	4	210K Ω 1% resistor	4.00
1	1K Ω multiturn pot.	1.00	2	390 Ω $\frac{1}{2}$ watt	.15
2	2K Ω $\frac{1}{4}$ watt resistors	.15	1	69.8K Ω 1% resistor	1.00
2	4.7K Ω $\frac{1}{4}$ watt resistors	.15	1	100K Ω	.10
1	10pF capacitor	.30	1	100 Ω	.10
			4	.5 Ω 1 watt resistor	1.00
			1	1 Ω 1 watt 1% resistor	1.08
			2	.003 μ F capacitor	.30
			1	330pF capacitor	.15
			2	6.2v 1N4735 zener diode	2.50

CONCLUSIONS

1. The DH design option is a viable alternative to the investment in expensive commercial potentiostats for use in corrosion research.
2. It is the only state-of-the-art mini-potentiostat known to regulate while supplying or sinking 1 ampere of current. (For a cost factor of two increase, it is presently believed that this unit could handle up to 5 amperes, momentarily, and 2 amperes, continuously.)
3. The data indicates that satisfactory regulation at higher current levels (>200 ma) leads to better regulation at small output currents (Δv vs. i linear). It is, therefore, concluded that circuits with large current capacity are desirable.

RECOMMENDATION FOR FUTURE WORK

Attempts at a comparison of the DH Potentiostat with commercial units under laboratory conditions will be made. Measurements of pit propagation rates in aluminum will form the first test case.

REFERENCES

1. Gileadi, E. et al, Interfacial Electrochemistry (Addison-Wesley, 1975), pp. 151-205.
2. Schroeder, R.R., "Operational Amplifier Instruments for Electrochemistry," Computers in Chemistry and Instrumentation v.2, ch. 10 (Marcel Dekker, Inc., 1972), pp. 263-350.
3. Schwarz, W.M. and Shain, I., Analytical Chemistry, Vol. 35, p. 1770.
4. Mansfeld, F. and Inman, R.V., Proceedings NACE Corrosion/78 Houston, paper number 168.

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