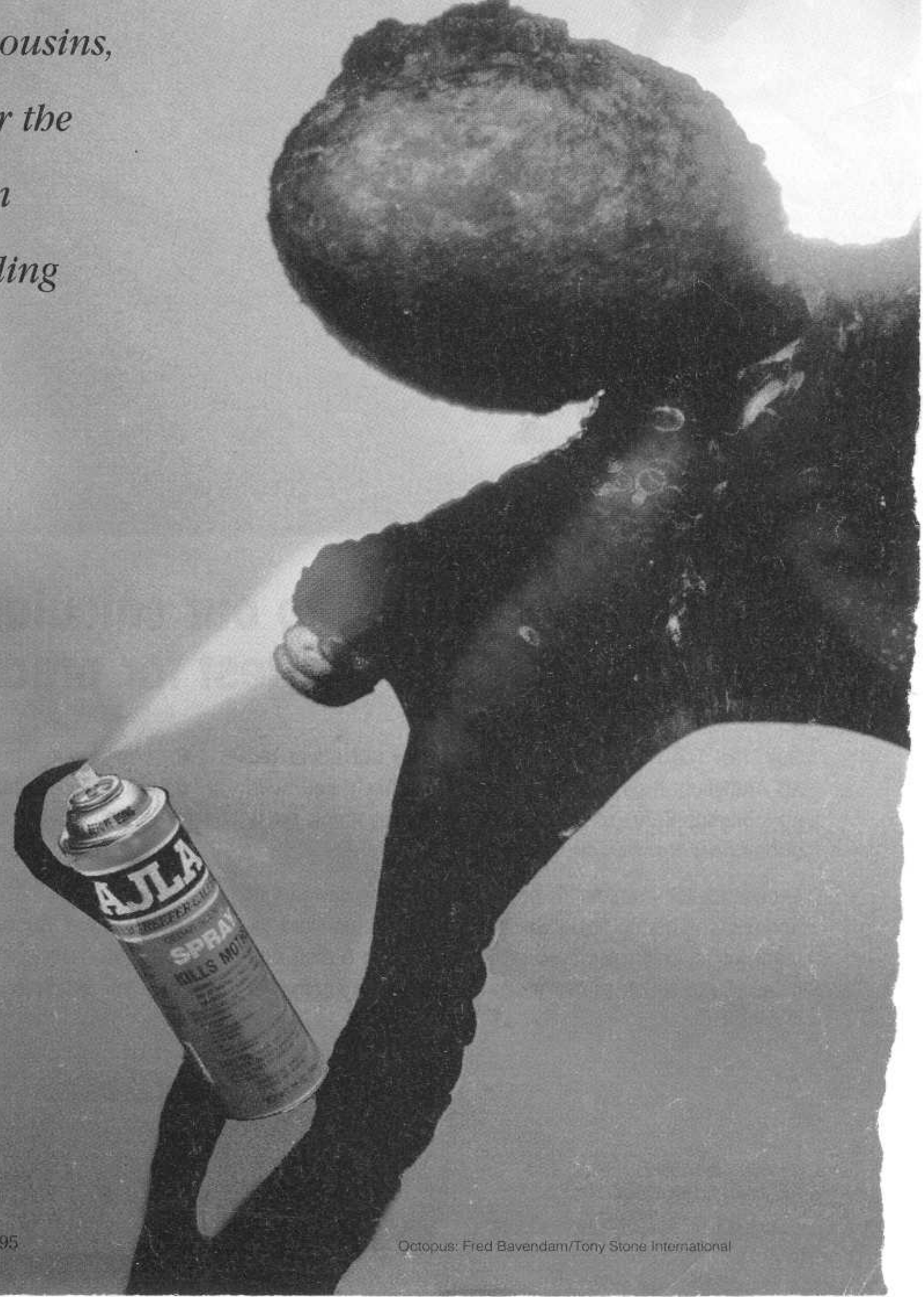
STALKING THE WILD POTENTIOSTAT

Robert S. Rodgers

Potentiostats and their cousins, galvanostats, are all over the place. Here's a primer on their uses, care, and feeding

It was, I think, Charlie Reilley, the legendary analytical chemist from the University of North Carolina at Chapel Hill, who first elegantly summarized electrochemistry as a four-dimensional relationship between current, potential, bulk concentration, and time. Although we rarely have control over time, almost all "dynamic" electrochemical experiments involve the control of either potential or current as well as measurement of the response of the other variable. As such, nearly all dynamic electrochemical experiments require the use of a potentiostat (to control potential) or its cousin, the galvanostat (to control current). What are these things? Why do we need them? What do we do with three- or sometimes even four-electrode connections? How do they work?

In what applications might you find a potentiostat or galvanostat in use? The answer is a great many, and varied ones at that. Small, low-powered potentiostats can be found in an analytical laboratory that does polarographic or voltammetric analysis for lead in drinking water or in blood. A potentiostat is incorporated in a pulsed electrochemi-



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cal detector that is being used to analyze sugars separated by LC. A simple, constant dc potential potentiostat can be found attached to a glassy carbon electrode for analysis of catecholamines or other neurotransmitters by liquid chromatography with electrochemical detection (LCEC).

High-frequency responding potentiostats are used by household products manufacturers to evaluate the protective coatings on the insides of aerosol cans by electrochemical impedance spectroscopy (EIS). Brewers use the same technique to evaluate how well the coatings on the inside of their cans protect a beer's taste and the integrity of the can. The research chemist might use a potentiostat to discover the mechanism of the oxidation of an aminophenol or to study chemistry in molten salts by square-wave voltammetry.

Higher power potentiostats can be found in a corrosion laboratory doing potentiodynamic scans on stainless steel samples, where the potentiostat is helping to evaluate the steel's resistance to pitting corrosion. High-current potentiostats are busy on semiconductor fabrication lines, etching silicon wafers. In analytical laboratories they may be used to do high-precision coulometric analysis for gold or other precious metals. They also have been used in the precise analysis of radioactive transuranium nuclides.

SIMPLE POTENTIOSTATS

The earliest electrochemical experiments were performed with a simple battery, a voltage divider, and only two electrodes. Current was measured with a sensitive microammeter, often a moving mirror galvanometer—the current rotated a mirror that reflected a spot of light onto a calibrated screen. The "automated" version offered a motor-driven voltage divider to scan potential. A piece of photographic paper, fixed to a rotating drum that was synchronized with the voltage divider, retained a permanent record of the current. This was the design of the Heyrovsky–Shikata polarograph (*1*), a far cry from the all-electronic, solid-state, computer-controlled potentiostats currently used.

Of those two electrodes from earlier times, one was the electrode of interest, or working electrode. The other served two purposes. It served as a reference electrode or a pseudo-reference electrode as well as the second electrode required to make a complete circuit. Two schemes were in common use. One was to build a large reference electrode—a classical saturated calomel electrode—of gargantuan proportions. Even drawing a few microamperes through this electrode could not change its potential. The other scheme was to use a large pool of mercury as a pseudo-reference electrode. Because the surface area of the pool was much larger than the area of the mercury drop electrode, the current density was effectively zero. Its potential was, therefore, essentially independent of the current. This scheme achieved the desired result: The experiment could be repeated in many laboratories with identical outcomes. The potential might not be derived from first principles, but at least it would be the same from lab to lab.

This simple, two-electrode arrangement suffices until the working electrode is made large, or until the current becomes large. In these cases, not all the voltage (energy) is available to make the desired electrochemical reaction proceed. Some of the voltage is wasted in overcoming the electrical resistance of the solution—it goes into making the electrolyte hot. This result can become a problem because the voltage determines which reactions will occur and which will not. If the available voltage changes, the outcome of the electrochemical reaction might also change.

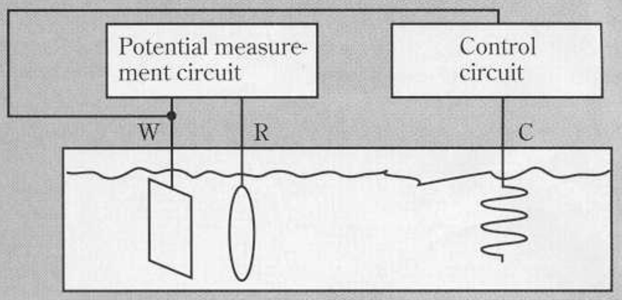
THREE ELECTRODES

The answer to the problem is, of course, to sense the electrochemically usable voltage and to adjust the applied voltage accordingly. Figure 1 shows this approach, using a working electrode, a reference electrode, and a counter electrode. The working electrode is connected to two different circuits. One measures the potential difference between the working electrode and reference electrode. The other is a power circuit that applies a voltage between the counter electrode and the working electrode and supplies whatever current is required.

If the measurement circuit reports that there is too little voltage between the reference electrode and the working electrode, the power circuit increases the voltage applied between the counter electrode and the working electrode. Likewise, if the measurement circuit reports that there is too much voltage at the reference electrode, the control circuit decreases the voltage applied between the counter electrode and the working electrode. The measure-and-correct nature of the process became clear to me the first time I used an electromechanical potentiostat. The measurement circuit's output drove a motor that quite literally turned the voltage adjustment knob on the power circuit. If the reference electrode-to-working electrode voltage difference was not correct, you could hear the motor making the correction.

Figure 1.

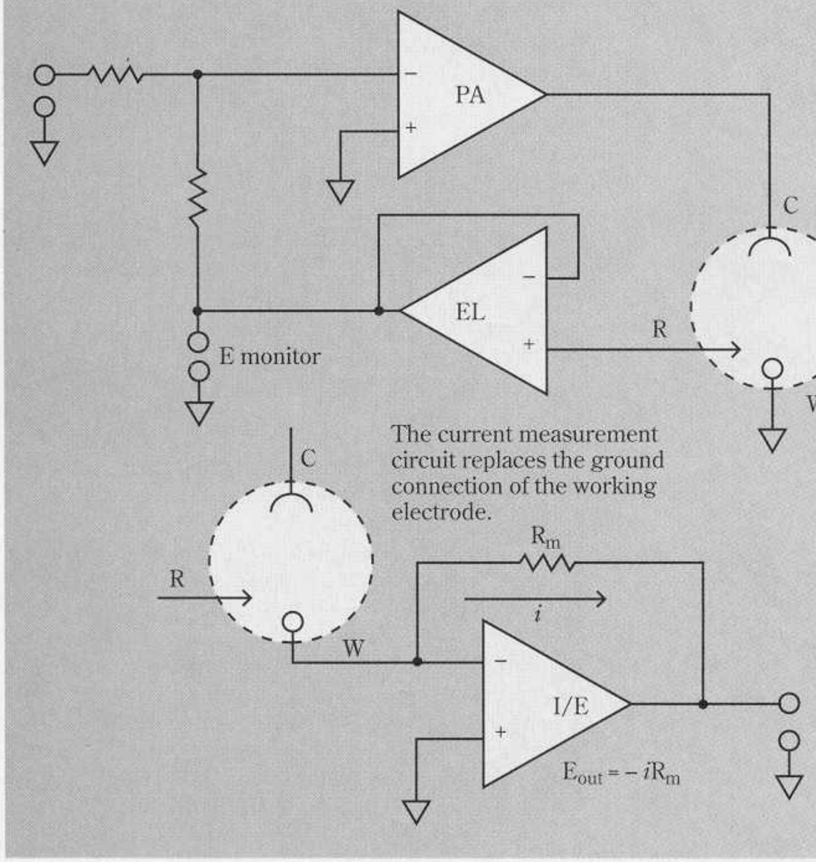
A SIMPLE POTENTIOSTAT



Working (W), reference (R), and counter (C) electrodes are connected to the measurement and control circuits.

Figure 2.

A SIMPLE "ADDER" TYPE POTENTIOSTAT SHOWING THE POWER AMPLIFIER (PA) AND ELECTROMETER (EL)



The current measurement circuit replaces the ground connection of the working electrode.

Current all-electronic potentiostats operate in much the same way. Figure 2 shows a block diagram for an electronic potentiostat (*2*). This simple potentiostat has two components. The first is the electrometer (EL), which fills the function of the measurement circuit of Figure 1 by reporting the potential of the reference electrode with respect to the working electrode, which is shown connected to the circuit ground, or zero voltage point (see Sidebar on p. 33).

Important characteristics of the electrometer are its maximum input voltage and its input impedance. The maximum input voltage is simply the highest voltage that can be applied to the reference electrode terminal of the electrometer without damaging the electronics. Commercial potentiostats are generally designed with some sort of protection circuitry to prevent permanent damage, but the operation of the electrometer will be compromised when the protection circuit is activated. Maximum input voltages are generally 10–15 V—adequate for nearly all common uses.

The input impedance is an important specification when the resistance of the reference electrode is high or when there are very good corrosion protection coatings. The higher the electrometer's input impedance, the better the electrometer is at sensing the reference electrode voltage without perturbing the cell. Input impedances range from 10^{10} to 10^{14} ohms.

The triangle labeled PA in Figure 2 represents the power amplifier or control amplifier of the electronic potentiostat. This circuit block's function is to control the potential difference between the working electrode and the reference electrode. It does this by changing the voltage on the counter electrode to correct for any deviations from the desired potential difference. It must do this independently of the amount of current required by the electrochemical cell. Two important characteristics of this amplifier are its maximum output current and its maximum output voltage.

The maximum voltage is generally called the compliance voltage of the potentiostat. For commercially available potentiostats, the compliance voltage ranges from 12 V to 100 V or more. The higher the compliance voltage, the larger the "wasted" voltage to be compensated for or overcome. A high compliance voltage is required when currents are large or when electrolyte concentrations are low, such as when working with low dielectric constant, nonaqueous solvents such as acetonitrile or dimethyl formamide (DMF). Don't confuse the compliance voltage of the potentiostat with the electrometer's maximum voltage rating. The compliance voltage is the maximum that might be present on the counter electrode, not on the reference electrode or at the electrometer.

The maximum output current of commercially available potentiostats ranges from several milliamperes to two or more amperes. The larger the maximum output current, the larger the working electrode can be or the higher the concentration of electroactive material that can be used. For work synthesizing new compounds, this translates into more material made per unit of time.

If the output voltage or the output current exceeds the design specification of the potentiostat, the working electrode-to-reference electrode voltage difference will not be the desired value. Often a potential overload or a control overload indicator will signal this problem.

MEASURING THE CURRENT

Another functional block of a potentiostat is the current measurement circuitry. Generally, the current passing through the cell is converted to a voltage signal by passing it through a resistor, R_m, and measuring the iR_m voltage drop across the resistor with a voltmeter. By changing the value of the resistor, the current range can be selected so that the iR_m drop matches the full-scale reading of the voltmeter.

The most common current measurement circuit is the virtual ground I/E converter (current-to-voltage converter) shown in Figure 2. The working electrode is no longer connected to ground but to the input of the I/E converter circuit, which has two jobs to perform. It converts a current, which flows into the circuit from the working electrode and out into a voltage that can be measured by a voltmeter. It also holds the working electrode at 0 V versus system ground, or at virtual ground. (It is called virtual ground because the potential of the working electrode is the same as that of the system ground, but there is no hard connection between them.)

GROUND—WHAT IS IT?

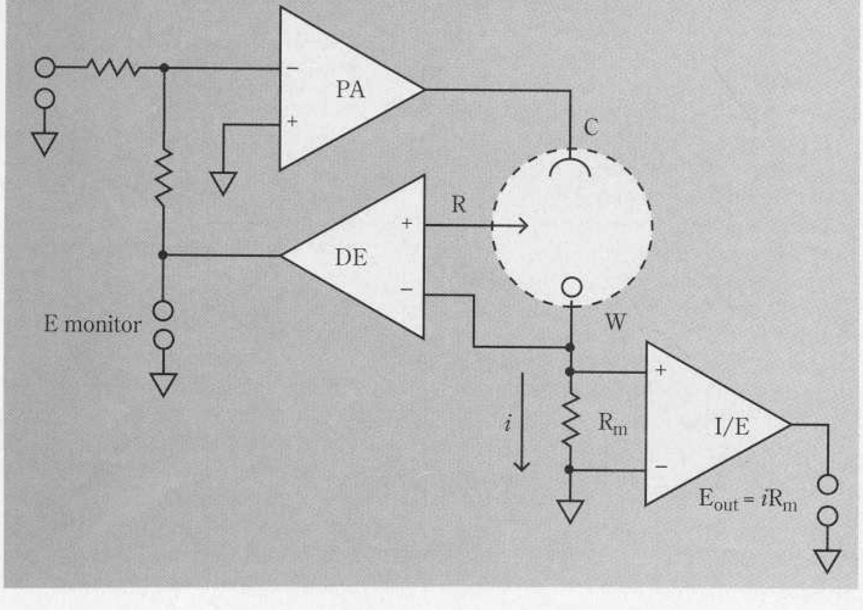
Often we refer to the "zero volts" reference point of a circuit as ground. This name arose because the reference point is often connected to the chassis of the instrument. For safety's sake, the chassis is generally connected to the earth through the third prong of the instrument's line cord. Never interfere with the grounding of an instrument's chassis by using a two-prong adapter or "cheater" cord. You may compromise the instrument's immunity to noise and certainly the user's safety.

Sometimes another part of the experimental apparatus may need to be connected to the earth. An example might be an autoclave used to elevate an electrochemical cell's temperature or pressure. In these situations a specially designed potentiostat is required, the ground of which is not connected to the earth. This is referred to as a "floating" instrument. Even a well-designed floating potentiostat is apt to be a bit noisier than one with a grounded chassis.

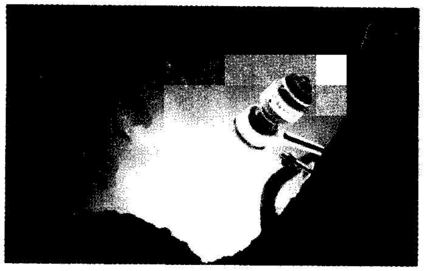
Ground is generally symbolized by a small inverted triangle. All of the ground symbols in a circuit are connected but, for the sake of clarity, this interconnection is not explicitly shown on the schematic.

Figure 3.

A POTENTIOSTAT WITH A PASSIVE I/E CONVERTER (I/E) AND A DIFFERENTIAL ELECTROMETER (DE)



Although the virtual ground I/E converter is generally thought of as the accepted way to make the current measurement, other architectures have been used. Figure 3 shows a diagram of a passive I/E converter and serves to introduce the topic of four-terminal or four-electrode measurements. Two changes have been made to the circuit design of Figure 2. The working electrode is no longer connected to ground or to a virtual ground. Instead, it is connected to one end of the current-measuring resistor, R_m. In this design the working electrode will be at a voltage (iR_m) that depends on the current flowing. The iR_m voltage drop across that resistor is sensed by the simple difference amplifier labeled I/E. Also, in Figure 3 the simple single-ended electrometer has been replaced with a differential electrometer (DE), so that the voltage difference between the reference and working electrodes can be sensed directly. This architecture has advantages when currents are high and the voltage drop across the connections to the electrode and through long wires may be significant (see Sidebar below).



Each architecture of potentiostat design has its own advantages and disadvantages. Some manufacturers have used both designs in different instruments (*3, 4*); others have designed a hybrid that uses the passive I/E converter for high currents and the virtual ground I/E converter for smaller currents (*5*). Some potentiostats combine the differential electrometer of Figure 3 with the virtual ground I/E of Figure 2 (*5, 6*).

The differential electrometer makes a kind of four-electrode measurement possible. The characteristics of a membrane may be studied by placing the counter electrode and the reference electrode on one side of the membrane and the working electrode and a second reference electrode on the other side. This second reference electrode is connected to the other (negative) input of the differential electrometer. Because the differential electrometer senses and reports the voltage difference across the membrane, the potentiostat can control this voltage.

SPEED AND STABILITY

Advances in microelectrodes and interests in EIS have fostered interest in faster electrochemical processes and have increased the demand for fast potentiostats. Evaluating the overall speed of a potentiostat can be tricky. Each of the three main circuit functions of the potentiostat—electrometer, power amplifier, and current measurement—will have its own impact on the overall speed (*7*). Reading the specifications for a potentiostat can be confusing. Very often the "rise time" is quoted, generally under "no load" conditions. This specification emphasizes the speeds of the electrometer and power amplifier.

More realistic is a system speed specification, which includes all three major circuit functions. This assesses not only how quickly the electrometer and power amplifier can respond to a rapidly changing signal (sine wave or square wave) and change the potential applied to the cell, but also how rapidly the I/E converter can respond to a fast-changing current. In most common uses, the limiting factor is not the power amplifier or electrometer but the current measurement circuit. In general, the more sensitive the current measurement, the slower it is. The 1-μA scale will respond more slowly than the 1-mA scale, and the 1-nA scale will be slower still.

Speed does not come without some associated problems. Manufacturers generally offer some selections for "bandwidth" or "compensation," which trade raw potentiostat speed for assurances that the system does not oscillate uncontrollably. The emphasis on the system is significant, because the stability (resistance to oscillation) is a function not only of the design of the potentiostat but also of the cell to which it is connected. Factors such as the construction of the reference electrode can play a major role in system stability.

SIGN CONVENTIONS AND THE POLARITY OF OUTPUTS

The electrometer (EL in Figure 2 or DE in Figure 3) isolates the reference electrode and provides an output that equals the reference electrode potential with respect to the working electrode. The electrochemist, however, likes to think of the voltage of the working electrode with respect to the reference. When the working electrode is at +1 V (with respect to the reference) the signal at the E monitor connector will read –1 V.

Things are even more confusing when talking about currents. Many American electrochemists think of a cathodic current (reduction at the working electrode) as positive; corrosion engineers, European electrochemists, and the remaining American electrochemists think of an anodic (oxidation) current as positive. For an anodic current, the virtual ground I/E converter in Figure 2 yields a negative output voltage; the passive I/E converter in Figure 3 yields a positive voltage. Check your instrument's manual!

COMPUTER CONTROL

Everything stated thus far about potentiostats applies wholly to analog potentiostats as well as to computer-controlled potentiostats. When we see what appears to be a digital potentiostat, it is really an analog potentiostat with digital or computer control. Digital-to-analog converters have replaced waveform generators and potentiometer knobs. Analog-to-digital converters have replaced oscilloscopes and strip chart recorders, but the basic analog potentiostat is still there underneath all the twenty-first-century lights and buttons.

If you want to get the most out of your computer-controlled potentiostat, be sure you have access to the analog potentiostat inside. Connectors for adding analog signals to a computer-generated ramp or staircase, as well as analog outputs for the raw current and potential signals, will enhance your potentiostat's versatility and guard against obsolescence.

Computer control helps us to automate experiments that used to be tedious and makes for better, more accurate measurements. With current autoranging, the potentiostat's microprocessor can make the decision about which is the best current range to use. Autoranging is particularly important in experiments such as a potentiodynamic scan where the current may change by factors of 10^6 (or more) during the corrosion measurement scan. It allows the chemist to focus on the meaning of an electrochemical experiment rather than on keeping the recorder on scale.

References

(1) Meites, L. *Polarographic Techniques*, 2nd ed.; John Wiley & Sons: New York, 1965.
(2) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980; Chapter 13.
(3) *Model 173 Instruction Manual*; EG&G Instruments, Princeton Applied Research: Princeton, NJ, 1991.
(4) *Model 273A User's Guide*; EG&G Instruments, Princeton Applied Research: Princeton, NJ, 1993.
(5) *Model 1287 Operating Manual*; Solartron Instruments, Inc.: Farnborough, UK, 1994.
(6) *Model 283 User's Guide*; EG&G Instruments, Princeton Applied Research: Princeton, NJ, 1994.
(7) Technical Note TN 201; EG&G Instruments, Princeton Applied Research: Princeton, NJ, 1994.

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