Technical Note 101

Subject: Potential Error Correction (iR Compensation)

INTRODUCTION

The PAR Model 273A potentiostat contains significant advances in state of the art potential error correction (iR compensation) circuitry. This technical note provides information necessary to understand both potential error correction in general and the advanced correction circuitry contained in the Model 273A.

GENERAL

In an electrochemical experiment, the voltage across the double layer of the specimen surface (E_{DL} in Figure 1) must be closely controlled. If you don't have confidence that the potential you are applying is the potential felt at the specimen, you can't be sure that the measurement is valid. However, there are factors that make it difficult to control E_{DL}.

The simplest case is illustrated in the following example. The equivalent circuit in Figure 1 represents an electrochemical cell connected to a potentiostat capable of controlling the potential between the reference and working electrodes (E_{CTL}). In all electrochemical cells, there is *some* resistance between the tip of the reference electrode and the outside of the double layer. This resistance is referred to as the *uncompensated resistance.* As current flows through the electrochemical cell, a potential is developed across the uncompensated resistance. The potential is calculated by:

$$E_{ERR} = I \text{ x } R_U \qquad \text{(Eq. 1)}$$

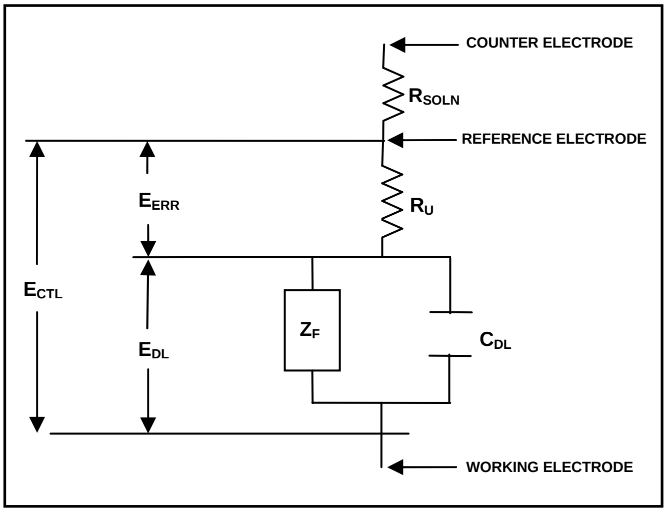

FIGURE 1: Simple model for electrochemical cell (Randles Cell).

When the uncompensated resistance gets high (as it does in pure water or organic solvents) or the current becomes large, a significant potential error may occur. Using this simple mode, the control potential is related to the potential across the double layer (the desired control potential) by this equation:

$$E_{CTL} = E_{DL} + E_{ERR} \qquad \text{(Eq. 2)}$$

Throughout the history of electrochemistry, electrochemists have tried to develop methods to eliminate the E_{ERR} term from equation 2, to produce this ideal equation:

$$E_{CTL} = E_{DL} \qquad \text{(Eq. 3)}$$

The most important of these methods are described in the following paragraphs.

Cell Design

Careful cell design can minimize the R_U value and thus minimize E_{ERR}. However, in many cases optimum cell design is restricted by other experimental requirements. In other cases, excessive cost or design complexity would be required to reduce the uncompensated resistance to a negligible value.

After-The-Scan Correction

If you measure R_U before the scan begins and then perform the scan, the potential value for each data point on the plot can be adjusted using the calculated E_{ERR} values. This approach has two drawbacks. First, R_U may change during the scan, causing error in the calculation of E_{ERR}. Secondly, since the correction occurs after the fact, the scan may not reach the desired final potential and the true scan rate may vary during the experiment.

Positive Feedback

At the beginning of an experiment, you make a manual or a computer-controlled feedback adjustment on the potentiostat. Once the adjustment is made, the potentiostat will automatically correct the applied potential as dictated by the measured current. This on-the-fly correction is an improvement over the previous method, since the values for the final potential and the scan rate are corrected. However, the correction is still based upon the *initial* value of R_U, which can change during the experiment. Also, this technique can cause severe stability problems when attempting to correct in a high speed system.

Current Interrupt

In many cases, this is the best solution to the R_U problem. The experiment is continually interrupted for a very short time (less than 200 µsec!). At each interruption, a new E_{ERR} value is determined and E_{CTL} is accordingly corrected so that the desired E_{DL} is maintained. Thus, the instrument has the ability to maintain the desired E_{DL} by increasing E_{CTL} to compensate for E_{ERR}.

The positive feedback and current interrupt methods of iR compensation are implemented in the Model 273A and are discussed in the following sections.

POSITIVE FEEDBACK

Introduction

Historically, positive feedback has been the most popular instrumental method of correcting the potential error due to uncompensated resistance. Figure 2 gives a simple representation of the positive feedback circuitry. In this simple circuit, the voltage output of the current-to-voltage converter is directly proportional to the current flowing through the cell. This voltage is applied to a voltage divider network (normally a front panel potentiometer) and a portion is fed back to the input of the potentiostat. Thus, the control potential is related to the applied potential and the uncompensated resistance by this formula:

$$E_{CTL} = E_{APP} + (\alpha \times i \times R_U) \qquad \text{(Eq. 4)}$$

α = proportionality constant determined by the ratio of the various resistors in the system.

E_{APP} = desired control potential.

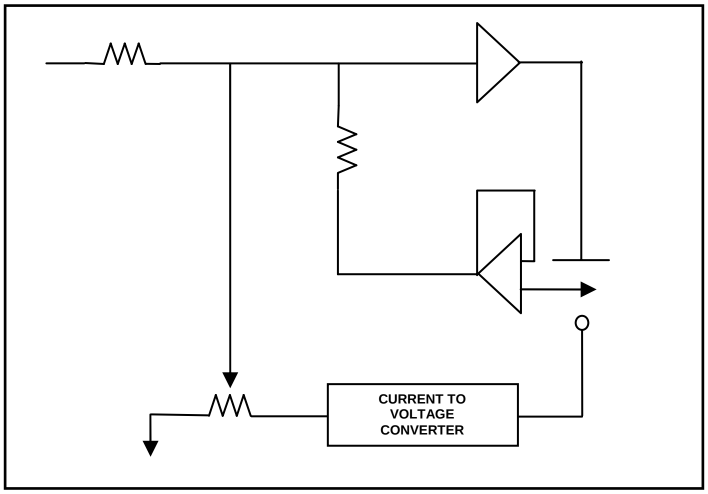

FIGURE 2: Simple positive feedback.

Substituting (E_{DL} + E_{ERR}) for E_{CTL} (from equation 2) yields this new equation:

$$E_{DL} + E_{ERR} = E_{APP} + (\alpha \times i \times R_U) \qquad \text{(Eq. 5)}$$

Rearranging to solve for E_{APP} yields the complete equation needed to adjust the applied potential:

$$E_{APP} = E_{DL} + E_{ERR} - (\alpha \times i \times R_U) \qquad \text{(Eq. 6)}$$

Equation 6 shows the complete relation between the applied potential, the double layer potential, the potential error and the uncompensated resistance. It is clear from this equation that you can properly adjust α to make the potential across the double layer equal to the applied potential.

Method of Adjustment

The adjustment of α is the critical step in positive feedback potential error correction. This adjustment is normally made in the following fashion:

1. The cell electrodes are adjusted and their positions fixed.
2. The cell is filled with the solution of interest and the potential is adjusted so that there is no electrochemical reaction.
3. A 50 to 200 Hz square wave of small amplitude (approximately 50 mV) is applied and the current waveform is monitored. See the Model 273A manual for details.

The design of the feedback circuit and the speed of the potentiostat determine the maximum possible α value. In many cases 100% feedback (α = 1) is impossible; severe system ringing or oscillation can prevent the potentiostat from maintaining control of the applied potential.

Setting the amount of positive feedback can be a confusing task, largely because the various types of experiments demand different degrees of compensation. In this light, two broad classes of experiments can be identified: "DC" experiments and "Fast Response" experiments.

DC experiments are those in which the potential at the electrode is changed slowly. One example of this involves the following steps: first you step the potential by a small amount; next you allow the transient effects of the step to subside; finally you measure the steady state (or DC) current. This type of experiment is common in corrosion laboratories. In a DC experiment, it is practical to compensate for nearly 100% of the potential error since the current measurement is made *after* the transient effects have subsided.

In Fast Response experiments, the potential is changed rapidly either in a ramp or in rapid steps. These experiments require some subjective judgment. An example of this class of experiment is potential step chronoamperometry. In this method, the chemist is interested in the shape of the current vs. time curve after applying a large potential step. If you compensate for more than about 85% of the potential error, you may get ringing in the current vs. time curve. If ringing occurs, you cannot make a valid current measurement until it subsides.

Advantage of Positive Feedback

The major advantage of positive feedback is that the correction is made in a continuous fashion (as opposed to current interrupt, where the current is periodically interrupted). Positive feedback must be used when a fast electrochemical experiment, such as cyclic voltammetry is being performed. In such an experiment, as the current changes the feedback changes proportionately and maintains E_{DL} as close to E_{APP} as possible. The time constant of this correction is dependent only on the electrical time constant of the feedback loop.

Feedback Loop Design

In most potentiostats, the positive feedback loop is designed so that the current range cannot be changed without degrading potential error correction capability. If the range is changed, the system is either overcompensated or undercompensated. In the Model 273A, the adjustment of both the feedback and the current range are controlled by a microprocessor. Thus, the current range can be changed and the feedback modified to reflect the change in current range.

(Note: The adjustment of the current range and the feedback network takes several milliseconds. Thus, in very fast experiments, the automatic current range feature should not be used.)

Figure 3 shows a block diagram of the positive feedback scheme in the Model 273A. In this system, the adjustment of the feedback is controlled by a multiplying digital-to-analog converter (or MDAC). The output of the MDAC is a percentage (from 0.025% to 100%, in 0.025% steps) of the input voltage (in this case the output of the current-to-voltage converter). The ratio of the positive feedback and the reference electrode resistors is 2 to 1. This makes the effective correction signal range from 0.05% to 200% of the feedback signal (in 0.05% steps).

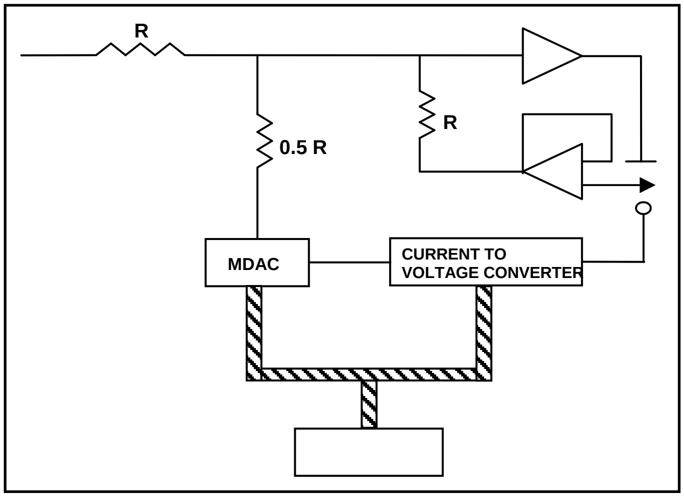

FIGURE 3: M273A positive feedback block diagram.

Ru and Current Range

The selected current range determines the degree of uncompensated resistance that may be offset. Within each range, you can compensate for a maximum of twice the value of the current measuring resistor in the current-to-voltage converter.

For example, when you select the 100 mA range, the maximum uncompensated resistance that can be offset is 20 Ω (see Table 1). You can't compensate for a R_U value larger than 20 Ω. However, this maximum R_U value will generate a potential error of 4 V (20 Ω x 200 mA).

Table 1 indicates the range and resolution of the correction for each current range. "Correction range" is defined as the maximum resistance that may be offset. "Resolution" is defined as the smallest increment in which the resistance can be programmed.

Current Range	Correction Range	Resolution
1 A	2 Ω	0.001 Ω
100 mA	20 Ω	0.01 Ω
10 mA	200 Ω	0.1 Ω
1 mA	2 kΩ	1 Ω
100 µA	20 kΩ	10 Ω
10 µA	200 kΩ	100 Ω
1 µA	2 MΩ	1 kΩ
100 nA	20 MΩ	10 kΩ

TABLE 1: Correction range and resolution for a given current range.

An Example of How Resolution Affects Correction

The resolution limit affects the accuracy of the programmed E_{CTL} value. For example, assume a resistance of 1.234 kΩ is entered on the 100 µA range. For that range, the resistance resolution is 10 Ω, giving an actual programmed resistance of 1230 Ω. In other words, the programmed resistance differs from the resistance entered from the front or rear panels by 4 Ω.

Let us continue with this example to see how errors due to exceeding the resolution limit can occur when you change the current range. If the current range changes to 1 mA during the experiment (assuming a resistance resolution of 1 Ω), the resistance actually used for correction will change to 1234 Ω. The improved resolution allows the R_U value that is actually used for correction to be identical to the entered R_U value.

A problem may occur when you shift to a more sensitive range. For instance, if you were to shift to a current range of 10 µA (and thus a resolution limit of 100 Ω), the resistance actually used for correction will be 1200 Ω. This is true because the value can only be represented to the nearest 100 Ω. In other words, the error will now increase to 34 Ω. Similarly, a further shift to the 1 µA current range would create an actual resistance of 1000 Ω (a 234 Ω error!) and a shift to 100 nA would create an actual resistance of 0 Ω (a 1234 Ω or 100% error!). Generally speaking, as the current range shifts to less sensitive ranges, the error will be accordingly reduced.

While it is important to understand the resolution of the feedback path, the maximum potential error that this represents is only 2 mV. In the above example, using the 10 µA range, the resistance error is 34 Ω. However, the error at this resistance is not catastrophic; even at the maximum current of 20 µA, the error is only 0.62 mV.

Summary of Advantages

Positive feedback has two major advantages, as described below:

1. Correction is continuous.

2. Correction is effective even when using the fastest scan rates possible with the Model 273A.

Summary of Disadvantages

While positive feedback is the only feasible technique when you want to use rapid scans (scan rates of 100 mV/sec or greater), there are some significant drawbacks, as described below:

1. The adjustment of the feedback is tedious and subjective.

2. The feedback reduces the stability of the potentiostat and may lead to severe ringing or oscillation.

3. Because the feedback signal affects system stability, it is normally not possible to adjust the potentiostat so that $\alpha = 1$. The user normally has to be satisfied with a potential error correction of α = 0.65 to 0.9.

4. When you make the initial feedback adjustment, you are assuming that the uncompensated resistance is constant. This can be an incorrect assumption. If R_U does vary, you will not be completely compensating for it.

CURRENT INTERRUPT

Introduction

An alternative to positive feedback is a system that periodically halts current flow to determine the actual value of the double layer potential (E_{DL}). Previous technologies, limited in processing capability and switching speed, made this method impractical. However, with the advent of microprocessors and modern switching techniques, it is now practical to incorporate a current interrupt method of potential error correction into commercial potentiostats. The Model 273A potentiostat uses such circuitry to perform current interrupt potential error correction (see the schematic in Figure 4).

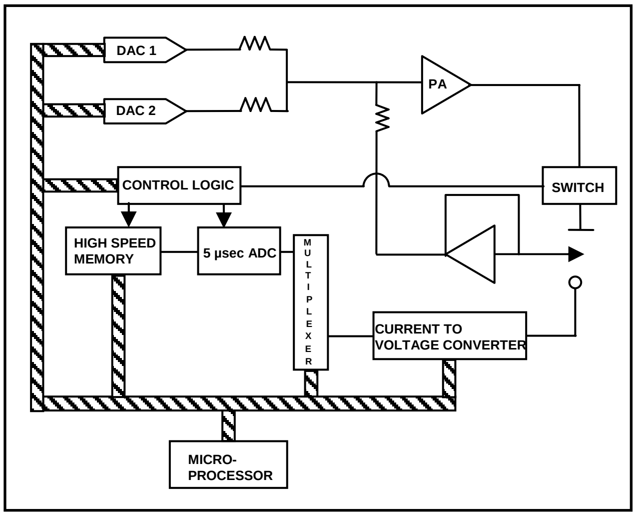

FIGURE 4: M273A current interrupt feedback block diagram.

Method of Operation

The current interrupt potential error correction circuitry used in the Model 273A operates as follows:

1. The desired potential is applied under control of the microprocessor (using DAC 1).

2. At a carefully selected time, the switch at the output of the power amplifier (PA) is opened, causing the current flow in the cell to go to zero.

3. Figure 5 is an ideal view of the reference electrode potential plotted vs. time. When the switch is opened, the error (E_{ERR}) in Figure 5 will become zero since no current is flowing. Thus, E_{REF} is controlled by the potential across the double layer (E_{DL}).

4. After the switch is opened, the potential across the double layer is determined by the rate of discharge of the cell. The rate of discharge is the product of the double layer capacitance (C_{DL}) and the general faradaic impedance (Z_F). The potential will vary exponentially.

5. The Model 273A measures E_{REF} every 5 µsec and stores that resulting data in a high speed memory. After 32 measurements the switch is closed and the potentiostat regains control of the cell. The total *off time* for each interrupt is less than 200 µsec.

6. Once the connection to the cell has been reestablished, the microprocessor reads the data out of the high speed memory and selects two data points (dependent of the current range of the I/E converter). It then calculates the intercept of the straight line through these two points at time zero (see below for details). The intercept point gives the value of the potential error (E_{ERR}) in the cell.

7. The E_{ERR} signal (up to ± 4096 mV at 2 mV resolution) is then applied to the cell using DAC 2. This correction cycle takes approximately 100 µsec after the cell is reconnected.

8. Finally, if a potential scan is underway, DAC 1 updates the control potential.

Note that this technique measures the potential error (the quantity of interest) and *not* the uncompensated resistance.

Theory

As we know from equation 2, E_{CTL} (the initially programmed potential) is normally the sum of E_{DL} (the desired potential across the double layer) and E_{ERR} (the error potential). After performing the above procedure, we have a measure of E_{ERR}. Equation 2 shows that if we continuously offset the control potential by the value of E_{ERR} we can maintain E_{DL} at the desired potential.

There is also an initial deviation to consider. When the correction potential is first applied, the current may increase, thus increasing the potential error. However, the next current interrupt cycle will detect this additional error and correct it. These iterations will continue for several cycles, until the error caused by the correction itself is smaller than the resolution of the correction.

In all cases, you can calculate the uncompensated cell resistance using Ohm's Law (E = iR) if you know the potential error and the current flow at the instant of interest. However, when you make this calculation, you must determine your values carefully. Ohm's Law dictates that at small current values, small changes in potential error represent large changes in uncompensated resistance. At 1 µA, a change of 1 mV represents a 1 kΩ change in uncompensated resistance!

Timing Considerations

There are some important timing considerations to be aware of when using current interrupt. First, the behavior of the reference electrode potential is determined by the RC time constant (a product of the double layer capacitance and the faradaic impedance). Secondly, the cell will not turn off in zero time, as the ideal waveform in Figure 5 shows.

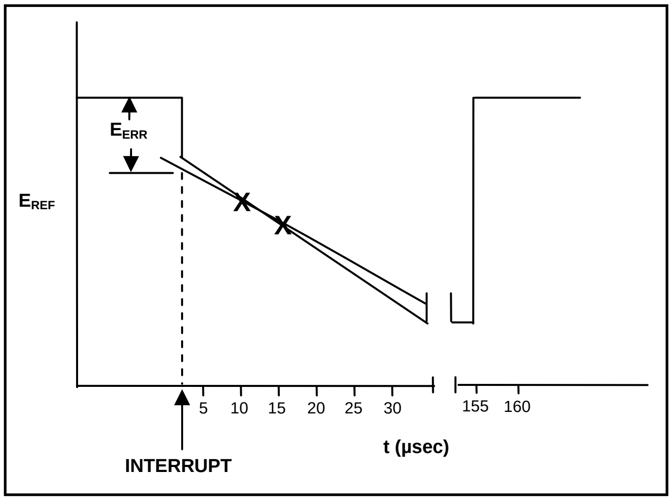

FIGURE 5: IDEAL voltage waveform for a current interrupt cycle.

For these reasons, you should choose your two data points carefully, keeping in mind these two important considerations:

1. The first data point must not be distorted by the cell turn-off.

2. Both points must be chosen early enough in the decay to ensure that the straight line approximation is valid.

From experience, we have determined a set of default data point times that are used with the Model 273A. Table 2 shows the values we have chosen for each current range. These values may be modified from the front panel of the Model 273A. See the Model 273A manual for further details.

Current Range	First Point Time	Second Point Time
1 A, 100 mA	10 µsec	20 µsec
10 mA – 100 nA	75 µsec	150 µsec

TABLE 2: Default values for data point times.

During operation, the timing of the current interrupt is determined by a value programmed from the front panel. This value can be set to any value between 4 msec and 30 sec, in multiples of 4 msec (the time base of front panel operation). If the entered value is not a multiple of 4 msec, the computer will round to the nearest 4 msec multiple. When no scan is applied, the correction cycles will occur under control of the front panel setting. (The default setting is one cycle per second.)

Data Acquisition Rate

When you try to program the data acquisition rate from the front panel of the Model 273A, there are several factors to consider. First, you must decide whether you want to synchronize data acquisition with the power line or not. If data acquisition is not synchronized with the power line, the time base will be 4 msec (that is, the microprocessor will process all parameters every 4 msec). If you choose line synchronization to prevent line related noise in the data, the time base will be 16.66 msec (20 msec for 50 Hz power).

The selected scan rate determines the rate at which the potential is updated. If the scan rate is less than 62.5 mV/sec, the potential is updated in 0.25 mV steps. The processor determines how many 4 msec intervals will occur between each step.

For example, using a 10 mV/sec scan rate, the potential should be updated every 25 msec. Since the time base is 4 msec, the update will occur three consecutive times at 24 msec and a fourth time at 28 msec. The 24 msec cycle will be divided into six 4 msec cycles. Five cycles will occur in which the current and potential are measured, but the potential is not changed. On the sixth cycle, the current and potential will be measured and the potential will be changed by 0.25 mV.

While the scan is in progress, the interrupt cycles are coupled with the potential update cycles. When the time between interrupts has elapsed, the interrupt is executed during the next data acquisition and potential update cycle.

Thus, while the potential is being scanned, each data acquisition and potential update cycle will occur in the following sequence:

1. The current will be measured.
2. The current interrupt cycle is executed.
3. The potential correction signal will be applied using DAC 2 (see Figure 4).
4. The applied potential will be updated using DAC 1.

Some care must be exercised in the timing of the interrupts. As the number of interrupt cycles increases, the percentage of time that the system is not controlled increases. Also, because of the nature of the measurement, the system noise will increase.

However, the larger the time between interrupt cycles, the larger the uncorrected error may become. This is especially true if the current is changing very rapidly. For example, in a corrosion experiment, the current can change by an entire order of magnitude during one cycle (when the scan is within a few millivolts of the corrosion potential). Thus, if the interrupt is occurring every 10 mV, erroneous potential may be applied to the cell.

Moreover, this system is really a positive feedback system with a long time constant (minimum of 4 msec) and a complex transfer function. Thus, special care must be exercised when choosing values which cause current interrupts to be widely spaced. For slow scans, interrupts occurring at one second intervals should yield good results.

An Example of a Current Interrupt Cycle

Figure 6 is an oscilloscope representation of a current interrupt cycle in an actual cell. In this illustration, the interrupt lasts 180 µsec and the cell turn-off time is very rapid. The upper trace shows the electrometer voltage waveform and indicates a potential error of approximately 1485 mV. The lower trace shows the I MONITOR output at a current of 85 mA. When full scale current output occurs (on any scale), the I MONITOR potential is always 1 V. Thus, using the 100 mA current range, an output potential of 850 mV indicates a current of 85 mA. Using the potential error and current values, you can calculate the uncompensated resistance using Ohm's Law. In this case, R_U is approximately 17.5 Ω.

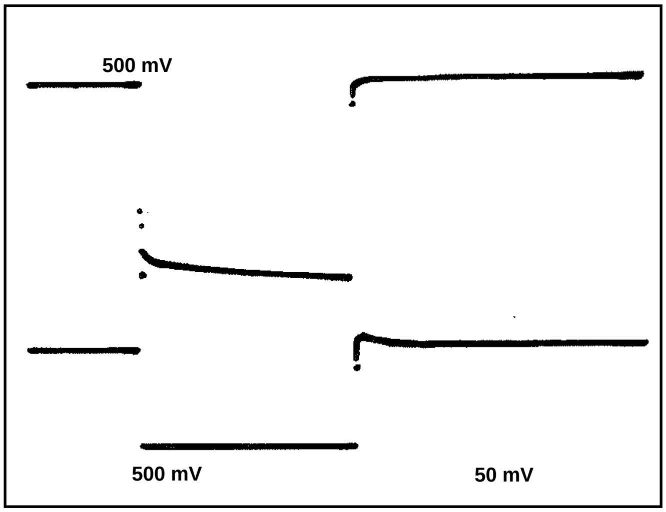

FIGURE 6: Actual current interrupt cycle.

In this example, the potential correction is 1485 mV. In order to maintain -935 mV across the double layer, it is necessary that the control potential be set at -2420 mV.

(Note: The value displayed on the front panel of the Model 273A can be either the actual control potential or the value of the voltage across the double layer.)

In many cases, especially when interrupts are performed frequently, you may have to use a modified reference electrode that has a better high frequency response. In this case, a platinum wire is placed at the tip of the reference electrode and coupled to the reference electrode using a small capacitor.[1,2] This allows the reference electrode to operate at high frequency and to respond to rapid changes in potential.

Summary of Advantages

1. Current interrupt will correct for virtually the entire potential error caused by the uncompensated resistance.

2. Current interrupt will correct for any changes in the uncompensated resistance as the scan progresses.

3. You have *no* adjusting to do. All you have to do is press a button to enable the correction.

Summary of Disadvantages

1. The correction occurs at finite times. Thus, current interrupt is not suitable for scan rates greater than 500 mV/sec and may not work properly at scan rates greater than 100 mV/sec.

2. If the correction is not updated frequently enough, the applied correction can be in error, although the error will not be as great as when no correction is made.

3. In some cases, this technique can cause the entire system to oscillate.

REFERENCES

1. Mansfield, F., et al, *Corrosion*, 38, (1982), p.570.
2. Hermann, C., et al, *Anal. Chem.*, 40, (1968), p. 1173.