Potentiostat stability mystery explained

Available instruments

Instrument	*MPG*	*VMP*	*VMP2*	*BiStat*
Used			´	
Alternative	´	´		´

INTRODUCTION

As the vast majority of research instruments, potentiostats are seldom used in trivial experimental conditions. But potentiostats are not only facing the unusual nature of the research activity, but also the great diversity of electrochemical systems and experiments. Even more, due to their nature, the electrochemical experiments evolve over extremely large ranges of values of the significant parameters. In corrosion applications, for example, recording the current over 5 or 6 current ranges in the same experiment is very common. It is not hard to imagine that, in such a demanding environment, potentiostats are often pushed to their limits and used in situations that may compromise their performance. There are always times when potentiostats are not functioning as expected. Ringing or oscillations, for example, are signs that a potentiostat has difficulties to maintain, or has even lost the control of the cell potential.

This document aims is to elucidate the origin of the stability problems of the actual potentiostats in close relation with the VMP2 multichannel potentiostat. Once you have better understanding of the instabilities you will be more confident to play with some experimental parameters like "bandwidth" or "current range" or chose a resistor value in series with the working electrode to settle down your potentiostat without loss of accuracy.

Although we will try to keep the text accessible, knowledge of potentiostats designs and terms like impedance, capacitance, Bode representation is recommended as well as basic skills on complex number calculus.

POTENTIOSTATS, BASIC PRINCIPLES

Since 1942, when Hickling built the first three electrodes potentiostat, a lot of progress has been done as to improve the potentiostat capabilities. Hickling had the genius idea to automatically control the cell potential by the means of a third electrode: the reference electrode. His principle has remaind the same until now.

At a glance, a potentiostat measures the potential difference between the working and the reference electrode, applies the current through the counter electrode and measures the current as an iR drop over a series resistor (R_m in the Figure 1).

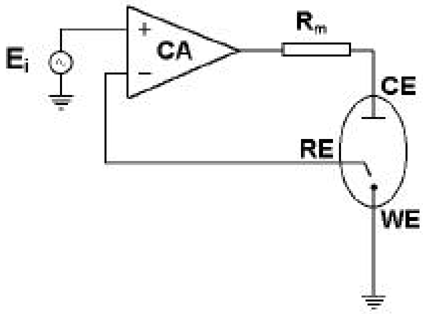

Figure 1 – Basic potentiostat design

The control amplifier CA is responsible to keep the voltage between the reference and the working electrode as close as possible to the voltage of the input source E_i. It adjusts its output to automatically control the cell current so that this equality condition is satisfied. To understand how it works we have to write down some equations very well known by electronics engineers.

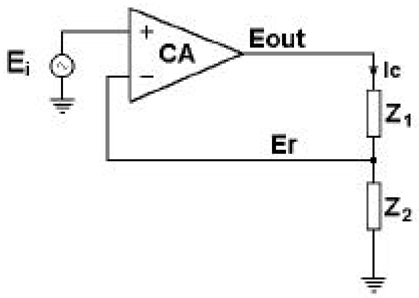

Figure 2 – An electrochemical cell and the current measuring resistor can be replaced by 2 impedances

Before going forward with maths note that from an electrical point of view the electrochemical cell and the current measuring resistor R_m can be regarded as two impedances (Figure 2). Z_1 includes R_m in series with the interfacial impedance of the counter electrode and the solution resistance between the counter and the reference. Z_2 represents the interfacial impedance of the working electrode in series with the solution resistance between the working and the reference electrodes.

The role of the control amplifier is to amplify the potential difference between the positive (or non-inverting) input and the negative (or inverting) input. This can be translated mathematically into the following equation:

$$E_{out} = A \cdot \left(E^{+} - E^{-}\right) = A \cdot \left(E_i - E_r\right) \qquad (1)$$

where A is the amplification factor of the CA.

At this point we should make the assumption that no or only insignificant current is flowing through the reference electrode. This corresponds to the real situation since the reference electrode is connected to a high impedance electrometer. Thus the cell current can be written in two ways:

$$I_c = \frac{E_{out}}{Z_1 + Z_2} \qquad (2)$$

and

$$I_c = \frac{E_r}{Z_2} \qquad (3)$$

Combining Equation 2 and 3 yields Equation 4.

$$E_r = \frac{Z_2}{Z_1 + Z_2} \cdot E_{out} = b \cdot E_{out} \qquad (4)$$

where b is the fraction of the output voltage of the control amplifier returned to its negative input; namely the feedback factor.

$$b = \frac{Z_2}{Z_1 + Z_2} \qquad (5)$$

Combining Equation 1 and 4 yields Equation 6.

$$\frac{E_r}{E_i} = \frac{b \cdot A}{1 + b \cdot A} \qquad (6)$$

When the quantity bA becomes very large with respect to one, Equation 6 reduces to Equation 7, which is one of the negative feedback equations.

$$E_r = E_i \qquad (7)$$

Equation 7 proves that the control amplifier works to keep the voltage between the reference and the working close to the input source voltage.

Where are those oscillations coming from?

Let's have a closer look to the control amplifier. Equation 7 is true only when bA is very large. Since the b fraction is always inferior to one this is equivalent to say that the amplification factor A must be very big. In practice, the control amplifier amplifies about 1,000,000 times the input difference voltage. In fact this is true only for low frequency signals. A real control amplifier is made of real, hence imperfect, components. Therefore it does not amplify in the same way a low and a high frequency signal. It is naturally to think that a slowly varying signal is amplified better than a high-speed signal. The control amplifier is more and more embarrassed as the frequency increases because it cannot catch-up with high-speed variation signals. So the amplification decreases as the frequency increase. Furthermore, the output signal is somehow shifted with regard to the input signal.

Obviously the amplification is a function of frequency, which can be expressed by a simplified mathematical model described by the complex Equation 8.

$$A(f) = \frac{a}{1 + j\frac{f}{f_a}} \qquad (8)$$

where f is the frequency, a the low frequency amplification, f_a is called the break down frequency and $j = \sqrt{-1}$.

As any complex number the amplitude can be expressed in polar form in terms of magnitude and phase:

$$A = |A| \cdot e^{j j_A} \qquad (9)$$

According to Equation 8 the magnitude is calculated as:

$$|A| = \frac{a}{\sqrt{1 + \left(\frac{f}{f_a}\right)^2}} \qquad (10)$$

and the phase as:

$$j_A = -arctg\left(\frac{f}{f_a}\right) \qquad (11)$$

Figure 3 shows the control amplification magnitude and phase plotted versus frequency for some common values of a and f_a . This graphical representation is very intuitive and very close to the real behaviour of the control amplifier. The amplification factor goes down for frequencies bigger than the break down frequency. When the amplification reach unity the control amplifier no longer amplifies, it becomes an attenuator. The frequency at which the amplification becomes unity is called the unity-gain bandwidth.

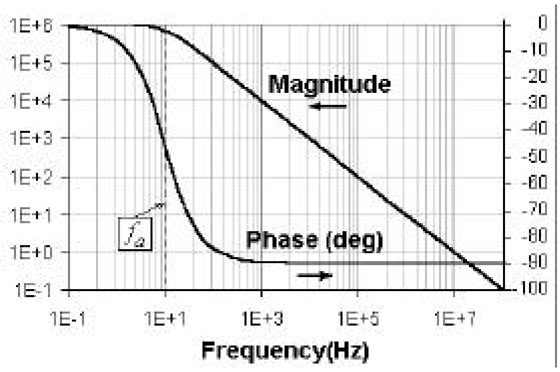

Figure 3 – Bode plot of the amplification magnitude and phase for $a = 10^6$ and $f_a = 10$ Hz

Now, let's go back to the Equation 6 and note that both the fraction b and amplification A are complex numbers. What is happening when the quantity bA approaches minus one?

$$bA = -1 \qquad (12)$$

Well, it is not difficult to see that the Equation 6 approaches –1/0, which points to minus infinity. In this case the control amplifier output heads to the power supply limit as fast as it can. When the limit is approached the control amplifier enters a nonlinear zone. At this point, it can either stay forever or head to the other power supply limit and so on until the power supply is disconnected. The second state is named oscillatory. In both states the potentiostat has lost the control of the cell and the system has become unstable. Note that the stability is determined only by the bA factor according to Equation 12. Thus a stability problem is exclusively due to the control amplifier characteristics, the current measuring resistor (included in *Z1*) and the cell. Nothing to do with the excitation signal!

Replacing the polar form of both b and A into the Equation 12 yields Equation 13.

$$|b| \cdot |A| \cdot e^{j(j_b + j_A)} = -1 \qquad (13)$$

which is equivalent with:

$$|b| \cdot |A| = 1 \qquad (14)$$

and

$$j_b + j_A = \pm 180° \qquad (15)$$

We have seen that the phase shift associated with the control amplifier can reach –90° for frequencies over the break frequency (see Figure 3). If the phase shift associated with the feedback is important then the total phase shift may reach –180°. If this occurs at frequencies where Equation 14 is satisfied then the system becomes unstable.

A very simple graphical method (also known as the Bode method) can be developed from Equations 14 and 15 to determine the stability of a potentiostat. Both $|A|$ and $1/|b|$ are plotted as a function of frequency on log-log coordinates as shown in Figure 3 and Figure 5. Equation 14 is fulfilled at the interception of the two curves. The total phase shift at the intercept can be determined by relating the phase shift to the slopes of the $|A|$ and $1/|b|$ curves. As shown in Figure 3 the magnitude rolls-off with a factor 10 within one decade of frequencies and the phase shift reach –90° for frequencies over the break frequency. Generally a negative magnitude slope of –10/decade corresponds to –90° phase shift while a positive 10/decade to +90° phase shift. Thus, if at the intercept point the $|A|$ slope falls with -10/decade and the $1/|b|$ slope rises with +10/decade then the total phase shift expressed by the Equation 15 gets close to -180° and the potentiostat is unstable.

PRACTICAL SITUATIONS

Connecting a highly capacitive cell to a potentiostat can be a troublesome experience especially when the application requires a sensitive current range. Generally things get worst on more sensitive current ranges. The reason is that this type of cell along with the current measuring resistor introduces important phase shift in the feedback signal.

Let's take a simply cell equivalent circuit for a nonfaradaic system (Figure 4).

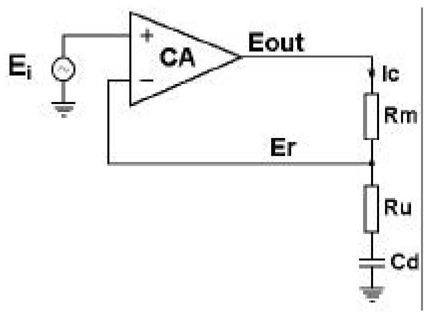

Figure 4 – Dummy cell for a nonfaradaic system

In this equivalent circuit the uncompensated solution resistance between the reference and the working electrodes is represented by the resistor R_u, C_d is the double-layer capacitance of the working electrode and R_m the current measuring resistor. The impedance of the counter electrode and the solution resistance between the counter and the reference electrodes have been neglected for the sake of simplicity (these impedances can be added in series with R_m for a more sophisticated analysis). For the Figure 4 circuit, the previously defined Z_1 and Z_2 impedances are expressed by the Equations 16 and 17.

$$Z_1 = R_m \qquad (16)$$

$$Z_2 = R_u + \frac{1}{j2pfC_d} \qquad (17)$$

Replacing terms in Equation 5 yields the feedback factor:

$$b = \frac{1 + j\frac{f}{f_2}}{1 + j\frac{f}{f_1}} \qquad (18)$$

where

$$f_1 = \frac{1}{2p\left(R_m + R_u\right)C_d} \qquad (19)$$

and

$$f_2 = \frac{1}{2pR_uC_d} \qquad (20)$$

Now let's perform the stability analysis by the Bode method, for some particular values of the dummy cell circuit (Figure 5). The amplification magnitude $|A|$ corresponds to the VMP2 control amplifier with the bandwidth factor set to 5. The $1/|b|$ quantity is calculated for C_d = 1µF, R_m = 100kΩ (10µA current range), R_u = 1kΩ (curve "b") and R_u = 0Ω (curve "a"). The frequencies f_1 and f_2 defined by the Equations 19 and 20 corresponds to the $1/|b|$ break frequencies.

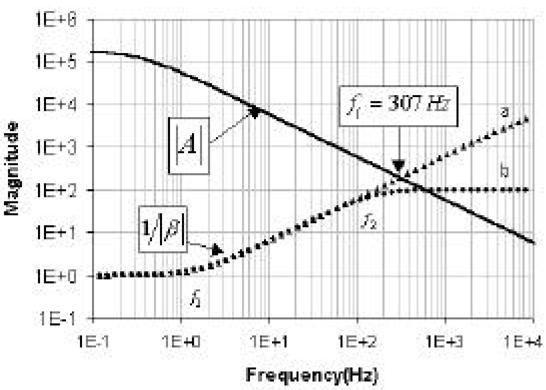

Figure 5 – Bode plots for Figure 4 dummy cell.
C_d = 1µF, R_m = 100kW, R_u = 1kW (b), R_u = 0W (a)

According to the Bode method the phase shift can be correlated to the slope of the $|A|$ and $1/|b|$ curves at the critical interception point. When R_u is set to zero the $1/|b|$ "a" curve has a slope of 10 by one decade of frequency and the $|A|$ curve has a –10/decade slope for about –180° total feedback phase shift at the interception point frequency (307Hz). This situation will cause oscillations. When the R_u = 1kΩ, the intercept point moves to a higher frequency where the $1/|b|$ "b" curve has a slope very close to zero. Under these circumstances the oscillation condition is not met, thus the system should be stable.

This stability analysis is in perfect agreement with the true behaviour of the VMP2 connected to this type of cell. Figure 6 shows a voltage step response of the system recorded with the EC-Lab software. Counter, counter sense and reference leads were stuck-together (CA1, REF3 and REF2) as well as the working with the sense lead (CA2 and REF1). In this test, the cell potential and current are recorded on the 10µA current range following a 100mV voltage step.

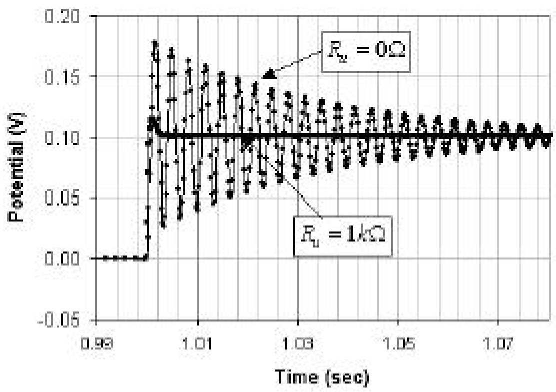

Figure 6 – Step response of the VMP2
for the Figure 5 dummy cell values.

Figure 5 predicts a stable state when $R_u = 1k\Omega$. Indeed, Figure 6 shows that the cell potential quickly reach the 100mV level with a small overshot following the voltage step made at 1.0 seconds.

Conversely, when R_u is set to zero, the system oscillate as expected. Well, here the oscillation does not last forever. The oscillation amplitude is attenuated in time and the system converges finally to the 100mV voltage level. Accurate calculation at the intercept point shows that the phase shift misses about 0.7° from the "perfect" –180° oscillation condition. It is interesting to note that the frequency of the oscillation matches the intercept point frequency. One can count about 6 periods in 20ms, which yields an oscillation period of 3.3ms thus a frequency of 300Hz.

As a parenthesis, potentiostats generally provide different *iR* compensation techniques to reduce the R_u solution resistance. Normally the *iR* compensation cannot completely remove the uncompensated resistance and often leads to instability problems. This behaviour can now be perfectly understood by the stability analysis prescribed in this note.

THE BANDWIDTH PARAMETER

To adapt to most of the practical situations, the VMP2 was designed with the possibility to change the control amplifier bandwidth. By changing the bandwidth one can “move” the system from an unstable state to a stable one. Seven stability factors (also called compensation poles) are proposed which correspond to the same number of bandwidths of the control amplifier. As a reference, the highest value (7) corresponds to the highest bandwidth of 680kHz and the lowest (1) to the lowest bandwidth of 32Hz. Intermediate values are shown Table 1.

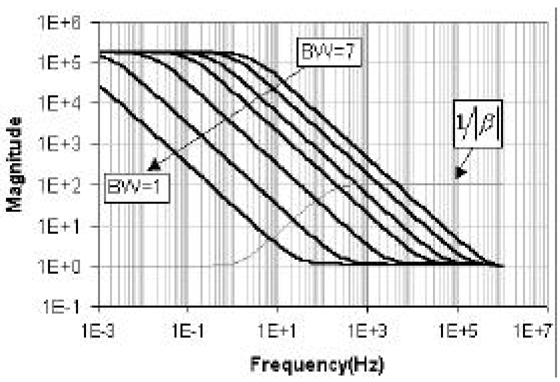

Figure 7 – VMP2 control amplifier bandwidths

Generally, the narrower the bandwidth (i.e. the lower the value), the more stable it gets, but this is not compulsory as can be shown in Figure 7. Sometimes the system may become stable when the bandwidth is increased, so if decreasing does not render the potentiostat stable, try to increase it.

Figure 7 shows, along with the VMP2 gain magnitude for the different bandwidth factors, the $1/|b|$ quantity for the previously defined dummy cell. As can be quickly seen, the system should be stable with the bandwidths factors 7, 6 and 5, it will probably manifest an important overshot with 4 and go into strong ringing or even oscillations for 3, 2 and 1.

STABILITY CRITERION FOR A CAPACITIVE CELL

A straightforward stability criterion can be deduced when the cell is a simple capacitance:

$$f_{BW} < \frac{I_{\max}}{4pC} \qquad (21)$$

where f_{BW} is the unity-gain bandwidth in Hz (see Table 1), C is the capacitance in F and the $I_{\max}$ is the maximum current of a current range in A.

Table 1 Bandwidth poles

Bandwidth factor	Pole frequency (f_{BW})
1	32Hz
2	318Hz
3	3.2kHz
4	21kHz
5	62kHz
6	217kHz
7	680kHz

Equation 21 yields to a simple abacus shown in Figure 8. To find the bandwidth factor for a stable system locate the intercept point of the capacitance with the desired current range. All the bandwidths on the right side of this point will provide stability.

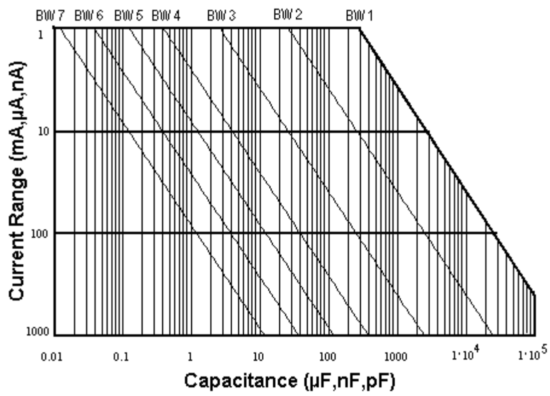

Figure 8 – VMP2 stability abacus; current range vs. capacitance: mA/µF, µA/nF, nA/pF

Examples:

1. C = 1nF, $I_{\max}$ = 10µA
   the stability can be acquired for BW5 - BW1
2. C = 1µF (1000nF), $I_{\max}$ = 100µA
   the stability can be acquired for BW2 - BW1
3. C = 10µF (10000nF), $I_{\max}$ = 10µA
   the stability cannot be acquired

If the stability cannot be acquired with one of the bandwidth factors a resistor should be added in series with the capacitance. A series resistor will have the same effect as the uncompensated solution resistance: it will stabilise the system but it will introduce an iR drop error. The resistor should have a minimum potential drop across it in order to have a minimum influence on the working electrode potential. A good compromise is to admit a maximum iR drop of 1mV.

The minimum resistor in series with a capacitance for a given current range and a given bandwidth factor is given by the Equation 22.

$$R_{\min} = \sqrt{\frac{2}{p \cdot f_{BW} \cdot I_{\max} \cdot C}} \qquad (22)$$

As an example, for C = 1000µF, $I_{\max}$ = 10µA and bandwidth 7 (f_{BW} = 680kHz) the stabilising resistor would be about 10Ω.

Note that higher the bandwidth smaller the series resistor value, thus smaller the iR drop error.

SETTLE DOWN THE POTENTIOSTAT

The first thing to do when your potentiostat gets mad is to admit that the cell might have its part of the responsibility. After all, the cell is part of the feedback element of the control amplifier. The rigorous way to find out what is happening is to draw a circuit model of the cell, compute the feedback factor b and use the Bode method for the stability analysis. This may be a difficult task since the electrochemical cells are seldom made of just simple capacitors and resistors.

If you want a quick solution to your problem without going into detailed stability analysis you may follow the next steps:

- Check your reference electrode. Make sure that the inside solution of the reference electrode has a good contact with the bulk electrolyte of the cell. If the porous junction is not wet then the electrode may have enormous impedance and together with the electrometer input capacitance may introduce a supplementary phase shift on the feedback.

- Change the Bandwidth factor. Start with a lower value. If decreasing does not work try to increase it.

- Chose a higher current range. Since the current measuring resistor is part of the feedback, the lower it is, the more stable the system gets. But there is a limit on how small a measuring resistor could be. If it is too small you won't be able to detect the low currents.

- If after the previous steps the system is still unstable, then you have to think about adding a resistor in series with the working electrode. When the cell is highly capacitive and you have an idea about the double layer capacitance then use Equation 22 to determine the resistor value.

- Reduce, if possible, the surface of the working electrode. Since the double layer capacitance is proportional to the electrode area lowering the surface will reduce the capacitance, which is generally responsible for the instabilities.

- Reduce also, if possible, the impedance between the counter and the reference electrode. This includes the interfacial impedance of the counter electrode and the solution resistance between the two electrodes.

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