IMP-1

MF-9065 INSTRUCTION MANUAL

Faradaic Impedance Module

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Table of Contents

Section 1. GENERAL INFORMATION

This manual describes the use and operation of the model BAS A.C. IMPEDANCE MODULE. This module can only be operated with the BAS 100B or the BAS 100B/W. The BAS 100B/Impedance Module system applies and analyzes sinusoidal A.C. waveforms in the frequency range of 0.1 millihertz to 1000 hertz. The details of this is given below in the Principles section.

Section 2. INSTALLATION

The AC Impedance Module consists of a small metal box containing the required circuitry mounted on a metal panel. The panel, in turn, mounts on the back of the C-2 Cell Stand/Faraday Cage. Mounting of the panel requires the unscrewing of the 4 thumb screws holding the existing panel in place, removal of the panel and replacing with the Impedance Module hardware.

Two electronic connections are required for the module to operate with the BAS 100B. One is the analog connection which is the cable with the two silver plugs (LEMO connectors) on either end. Plug one of the connectors into the CELL port on the BAS 100B and the other into the appropriate port on the Impedance Module. The second is the control connection which is a 37 pin grey ribbon cable that connects into the ACCESSORIES port on the BAS 100B and the 37 pin socket on the Impedance Module. When these connections are made the instrument is ready for Initial Calibration. See this section below for details. If initial calibration has already been done then the instrument is ready to operate as described in the Operations section below.

Section 3. PRINCIPLES

A Faradaic Impedance measurement is used to obtain electrode process, kinetic-mechanistic information about an electrochemical system. This is done by applying a small amplitude, alternating sinusoidal waveform to the system when it is at equilibrium or steady state. Under these conditions the response is considered linear and, as such, data are analyzed by usual AC electronic circuit methods. In addition, since the electrochemical system is not changing, data can be collected over long times thus the measurement is of high quality, low noise and high precision.

Since Faradaic Impedance data is generated and analyzed in a similar fashion to electronic impedance data, analogies are commonly made between the electrochemical system and an electronic circuit. These equivalent electronic components have nothing to do with the electrochemical phenomena but they are useful to gain some insight into the physico-chemical actions actually occurring in the system.

Electrochemical processes that inhibit or impede the applied AC potential waveform are equivalent to solution or other ionic resistance, Faradaic reactance (charge transfer resistance), double layer or other capacitance, pseudo-inductance, mass transfer limitations and any variable that would affect these.

The Faradaic Impedance experiment is a measurement of time dependent events at one energy (potential) value. This is in contrast to a voltammetric experiment where a large energy spectrum is examined at one time. Data analysis is able to decipher events occurring in microseconds (even sub-microseconds in some cases) to years. Applications might run the gamut from the time required for the non-Faradaic solvent reorganization process following an electron transfer to the oxidation of a steel bridge occurring over decades of years.

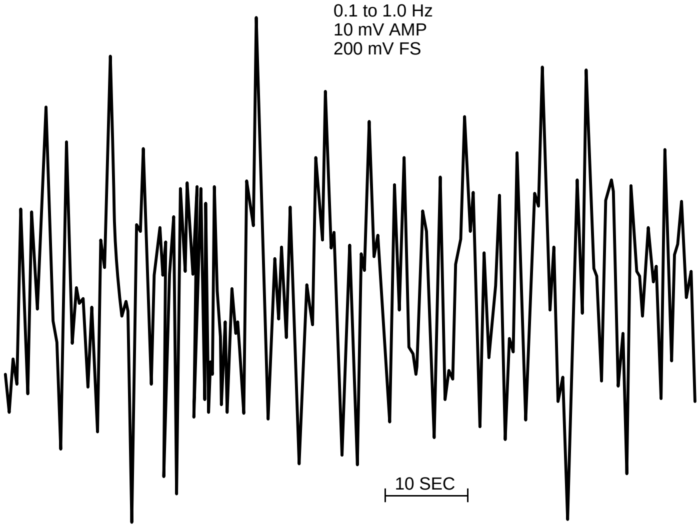
This instrument is designed to examine the relatively slower, longer time, lower frequency electrochemical or other physical processes. The frequency range is 0.1 millihertz to 1 kilohertz or it is able to measure phenomena in the 1000s of seconds range to millisecond times. This corresponds to approximate electrochemical rate constants, k(sh), of <0.1 cm/sec.

A typical AC impedance experiment collects data for one frequency at a time. This is a very time consuming operation considering a study would cover many decades of frequency range and, perhaps, a few hundered millivolts of potential range. Let alone the time considerations to collect and tabulate the data, what is happening to the electrode? Is it the same for the last experiment as it was for the first? Considerable time could be saved if many frequencies could be applied and analyzed simultaneously. This is what is done in this instrument though for only one decade of frequency range at a time. A broader range could be done simultaneously but, in practice, data quality suffers. This is discussed in more detail in the Practical Considerations section below.

This instrument incorporates what might called a “Fourier” method for both waveform generation and data analysis. In the frequency domain, many frequencies of equal amplitude and random phase are choosen such that the ratio of one frequency to the next is the approximately the same which yields a relatively equally spaced frequency test set and furthermore this assures one frequency is not a harmonic of another. This is somewhat different from Professor Don Smith’s odd-harmonic pseudo-random white noise (Smith, D.E., Anal. Chem., 48(1976) 221A-240A) spectrum though it still meets the same criteria.

The frequency components used for one decade are: 12, 15, 19, 23, 28, 35, 44, 55, 73 and 95; 10 frequency components. They are evenly spaced within the decade covered with a ratio of 1.25 between adjacent frequencies. There are no harmonics and the power line frequencies of 50 or 60 Hertz are avoided. Again, in the frequency domain, they are of equal magnitude and of random phase. These are then transformed into the complex plane and an inverse Fourier Transform function is applied to give a digital representation of a time domain waveform. This is sequentially run through a D/A converter and analog filters and applied to the cell. For signal-to-noise improvement, this procedure can be repeated for as many cycles as desired. An example of the applied waveform is shown in Figure 1.

Figure 1. An example of the white noise waveform used for A.C. Impedance technique. Frequency range: 0.1-1.0 Hz. A.C. Amplitude: 10mV.



The response is monitored by a current transducer whose sensitivity range is automatically adjusted for each frequency range examined. One cycle is run and then depending on the response, the range is increased or decreased if needed. As mentioned above, multiple cycles are run to improve signal-to-noise and each cycle is noted by a period (a dot) on the screen of the 100B. This is used as an indicator of run progress. Experiments may require many hours to complete so knowing how many cycles have been run in a particular frequency range is useful information.

After each frequency range is completed, the Fourier Transform algorithm analyzes the data. The results are the phase and amplitude relationships between the applied A.C. potential and the output A.C. current response. This information is then used to determine the cell impedances (or admittance, the reciprocal of impedance) which relate to the cell variables like; cell uncompensated resistance, Faradaic impedance (finite heterogeneous rate constants), double layer capacitance, etc.

The results are presented in numerous transformed data displays to ease analysis. There are 14 different output plots available in this instrument. They are:

1. Z" - Z’ (Nyquist Plot)
2. Y" - Y’
3. LOG Z - LOG(FREQ) (Bode Plot)
4. LOG Y - LOG(FREQ)
5. PHASE - LOG(FREQ) (Bode Plot)
6. Z" & Z’ - LOG(FREQ)
7. WZ" - WZ’
8. WY" - WY’
9. Z"/W - Z’/W
10. Y"/W - Y’/W
11. Z’ - WZ"
12. Z’ - Z"/W
13. Z" & Z’ - 1/SQRT(W)
14. COT(PHASE) - SQRT(FREQ)

SQRT = Square Root
Y = Amplitude, Admittance
Y" = Imaginary Part, Admittance
W = Angular Frequency
Z’ = Real Part, Impedance
COT = Cotangent
Y’ = Real Part, Admittance
FREQ = Frequency
Z = Amplitude, Impedance
Z" = Imaginary Part, Impedance

Section 4. TYPICAL APPLICATIONS

A.C. Impedance measurements are currently very popular for studying electrochemical systems. This technique has been called “High Tech Electrochemistry”. It is true Impedance data yields a great amount of information about the system being investigated but the difficulty is interpretation. Regardless, like any other electrochemical technique, there are many important applications where impedance measurements have an advantage.

The applications of this impedance measurement system revolve around electrochemical systems where the heterogeneous rate constants are less than 0.01 cm/sec and corresponding equivalent impedance values are no less than 10E9 ohms. For example, many organic electrochemical reactions fall into these categories. Studies can be done on electrodes that have films on them, electroactive or not, that are used for analytical or anti-corrosion purposes. Fundamental corrosion processes can be studied.

Since resistive and capacitive (and inductive) effects can be measured, any process that would affect these variables would be an application. Studying the effects of surfactants on an electrode might be one example.

Section 5. INITIAL CALIBRATION (100B)

The instrument must be calibrated with a reference impedance value before operation. This procedure places a calibration table in battery backed RAM so once it is done it does not have to be repeated as long as the batteries are functional. This calibration is usually done in the factory before the instrument is shipped but, if the analyzer was upgraded at some time or the batteries failed, then the instrument has to be re-calibrated.

This permanent calibration is done by using a 1000 ohm (it must be 1000 ohms!) resistor as the cell. The resistor is placed between the working electrode lead on one side and the auxiliary and reference electrode leads on the other side of the resistor connector wires. The INITIAL potential must be zero, 0. Then, at the Star, *, prompt, the command REFERENCE is entered. This command calibrates the entire frequency range and requires many hours to complete, e.g., one cycle at 10E-4 hertz requires 10,000 seconds or about 3 hours. As a suggestion, start the calibration in the evening and let the process happen overnight which will make it ready to run the following morning.

PROMPT	RESPONSE	DESCRIPTION/COMMENTS
*	REFERENCE↵	Calibrates the entire frequency range to a 1000 ohm resistance. Calibration table placed in battery backed memory so it needs to only be done once.

(Progress will be indicated by noting the frequency range being calibrated and the cycle which is being processed by a period or dot per cycle. For example, four dots would indicate 4 cycles have been completed.)

Section 6. INITIAL CALIBRATION (100B/W)

Before any IMP experiments can be run, the BAS 100B/W must be calibrated. This is done using the Other Item under the Control Menu.

There are 3 important features in this Dialog Box: 2 Command Button and 1 pair of Option Buttons. The 2 Command Boxes, “Reference” and “Calibration” are the 2 ways of setting the calibration. Both methods require a 1000 ohm resistor, which is connected to the working electrode lead on one side and the reference and auxiliary electrode leads on the other. The Init E in the General Parameters (see below) must be set to 0 (this is the default value). The “Reference” Command calibrates the entire frequency range, using the default parameters. The results are stored in a calibration table in battery backed RAM, so the procedure does not have to be repeated for the lifetime of the battery. This calibration requires many hours, so is best done overnight. If the Impedance Module was purchased with the BAS 100B/W, then this calibration was done in the factory before shipping. If not, then this calibration must be done by the user.

The Calibration Command generates a special calibration table to be used under a given set of user-defined conditions (e.g. frequency range, amplitude). However, this calibration table is not stored in battery backed RAM, and is lost when the main power is switched off. When this table is set up, it automatically overrides the table stored from the Reference Command, and this is shown by the On Option Button in the Calib box. This table can be disabled by clicking the Off Option Button.

Section 7. OPERATION (100B)

PROMPT	RESPONSE	DESCRIPTION/COMMENTS
OPERATION MODE:	IMP↵	IMPedance technique.
INIT E(MV)=#	↵ or -3276 to 3276 ↵	INITial or the applied potential, E, in MilliVolts, Default: 0
LOW FREQUENCY (HZ)= 1.0E#	↵ or -4 to 2↵	LOWest FREQUENCY to be examined in HertZ Default: 1
HIGH FREQUENCY (HZ) 1.0E#	↵ or -2 to 3↵	HIGHest FREQUENCY to be examined in HertZ. Default: 3
A.C. AMPLITUDE (MV)=#	↵ or 1 to 250↵	Amplitude of the applied AC potential waveform in MilliVolts Default: 5
AVERAGING CYCLES=#	↵ or 1 to 2048 ↵	Number of CYCLES AVERAGED per data point (set). Default: 16. The larger the number, the less noise but longer times per run.
SENSITIVITY (A/V)=1.0E-#	↵ or 0 to 7 ↵	Current-to-Voltage Converter gain in Amperes/Volt output, Default: 0 (Automatic gain ranging).

Section 8. STAR COMMANDS (100B)

The following are the Star Commands specific or unique to the Faradaic Impedance technique.

PROMPT	RESPONSE	DESCRIPTION/COMMENTS
*	CS↵	Change Specific parameters
QUIET TIME (SEC)=#	↵ or 0 to 65535↵	The TIME between starting the run, i.e., R↵, and the actual start of the experiment. The electrode is connected during this time. Default is 15.
FREQUENCY RANGE (0=1DECADE, 1=2DECADES)=#		Enter the number of decades to examine per cycle. Default: 1 decade.
*	B↵	Choice of data display placed on video screen or plotted.

DATA DISPLAY OR PLOT MODE:

1. Z" - Z’ (Nyquist Plot)
2. Y" - Y’
3. LOG Z - LOG(FREQ) (Bode Plot)
4. LOG Y - LOG(FREQ)
5. PHASE - LOG(FREQ) (Bode Plot)
6. Z" & Z’ - LOG(FREQ)
7. WZ" - WZ’
8. WY" - WY’
9. Z"/W - Z’/W
10. Y"/W - Y’/W
11. Z’ - WZ"
12. Z’ - Z"/W
13. Z" & Z’ - 1/SQRT(W)
14. COT(PHASE) - SQRT(FREQ)

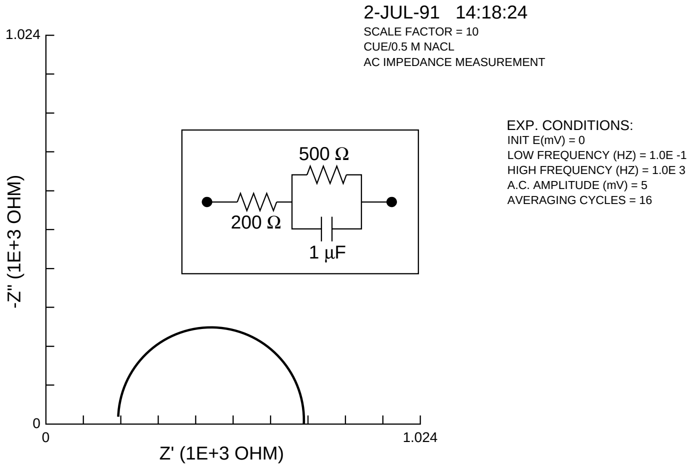
SELECTION = #	↵ or 1-14↵	Enter the number of the desired plot from the above list.
QUADRANTS (0=1, 1=1&4, 2=1&2, 3=ALL)=#	↵ or 0-3↵	Enter the number of the desired quadrants to be displayed or plotted. Cartesian format.
DATA TYPE (0=MAIN, 1=G, 2=Z)=#		Choice of displaying or plotting MAIN memory data, stored background data (G data) or background subtracted data (Z data).

(If 0 or 1, then video display or plot) (If 2, then

MODEL (0=SERIAL, 1=PARALLEL)=#	1 or 2↵	Choice of subtracting the stored data from MAIN memory data in either a Serial or Parallel fashion. Use with caution. Works well with electronic RC networks but may not be effective for electrochemical systems.

(The impedance plot format is different than other plots. It has a much larger dynamic range. The Scale Factor (SF) number is, in this format, equal to n where n is the binary exponent, i.e., 2^n. This allows ranges from as little as 1 ohm full scale to 10^12 ohms full scale in some cases. When using the FREEZE command, changing the scale factor by one number will increase or decrease the size of the plot by a factor of 2. For example, if the FREEZE scale is choosen 4 numbers away from the SF number, the display or plot size will change by 2^4 or 16. Also, when the units of the X and Y axis are the same, the range displayed for both axis is the same. If the units are different, then the FREEZE function will operate only on the Y axis data.)

Figure 2. Examples of Nyquist Plot (Z" vs. Z').



*	CALIB↵	This generates a special calibration table to be used under a given set of conditions; specific frequency range, amplitude, etc. It assumes a 1000 ohm resistor is being used as the cell. This is like the REFERENCE command above, but calibrates for the experimental conditions stated. This overrides the REFERENCE table. Disabled with the NCALIB command.

(Video display will show calibration run progress.)

*	V↵	Present a table of the impedance results.
TYPE (0=IMPEDANCE, 1=ADMITTANCE)=#		Choice of presenting Impedance or Admittance data.

```
BASE FREQUENCY = ### HZ

                                              IMPEDANCE
HARMONIC        REAL            IMAG        (ADMITTANCE)     PHASE
    12        +####E+#       +####E+#       +####E+#        +##.##
    15        +####E+#       +####E+#       +####E+#        +##.##
    19        +####E+#       +####E+#       +####E+#        +##.##
    23        +####E+#       +####E+#       +####E+#        +##.##
    28        +####E+#       +####E+#       +####E+#        +##.##
    35        +####E+#       +####E+#       +####E+#        +##.##
    44        +####E+#       +####E+#       +####E+#        +##.##
    55        +####E+#       +####E+#       +####E+#        +##.##
    73        +####E+#       +####E+#       +####E+#        +##.##
    95        +####E+#       +####E+#       +####E+#        +##.##

BASE FREQUENCY = ### HZ
    (etc)
```

*	COR↵	CORrection for the effects of uncompensated resistance and/or double layer capacitance.
R(OHM)=0	###	Enter the amount of resistance to subtract.
C(NF)=0	###	Enter the amount of capacitance in nanofarads to subtract.

(On any following displays or plots, i.e., the B command, the corrections as given with this command will be applied to the data. Excercise with caution!)

*	ERASE↵	This command gives the option to ERASE or not ERASE all previous results when a second experiment is run. The purpose of this command is that it allows a particular frequency range to be run a second time without erasing the previous experiment's data. It also allows ERASing of a specified decade of frequency range without affecting other data from the run. This only applies to data that would not be replaced by data from a new run, i.e., all new data erases existing data.
ERASE (0=NO 1=YES 2-IMMEDIATE)=#	1↵	Enter the number corresponding to the desired condition. If 1 is entered, the old set of data will be erased if the new experiment does not cover the same frequency range. This is the default condition.
	0↵	If 0 is entered, then all old, existing data will not be erased when the next experiment is run.
	2↵	If 2 is entered, then one set of data corresponding to one or two decades of applied frequency range is erased.
NUMBER (1-9)=#	1 to 9↵	The numbers 1-9 represent the frequency ranges; 0.0001-0.01, 0.001-0.1, 0.01-1.0, 0.001-0.01, 0.01-0.1, 0.1-1.0, 1.0-10, 10-100 and 100-1000 Hertz respectively. This acts on the data only once. The ERASE status returns to the original status, 0 or 1.

Section 9. OPERATION (100B/W)

Mode = IMP

General Parameters

Init E (mV) = 0	-3276 to 3276
Low Frequency (Hz) = 1E 1	-4 to 2
High Frequency (Hz) = 1E 3	-2 to 3
A.C. Amplitude (mV) = 5	1 to 250
Sensitivity (A/V) = 1E-6	1 to 7

Special Parameters

Frequency Coverage (decade) = 1	1 or 2
Quiet Time (sec) = 2	0 to 65535
Cycles 100-1000 Hz = 64	1 to 400
Cycles 10-100 Hz = 16	1 to 400
Cycles 1-10 Hz = 16	1 to 400
Cycles 0.1-1 Hz = 8	1 to 400
Cycles 0.01-1 Hz = 8	1 to 400
Cycles 0.01-0.1 = 2	1 to 400
Cycles 0.001-0.1 = 2	1 to 400
Cycles 0.001-0.01 = 1	1 to 400
Cycles 0.0001-0.01 = 1	1 to 400

Comments:

1. The A.C. Amplitude should be 8/n mV or less (n = number of electrons).

2. In the two lowest frequency decades, each cycle requires ca. 3 hrs. Therefore, no more than one cycle should be used since the system may change significantly over the time period of the experiment. If the system is relatively unstable, it may not be possible to use these decades at all.

Display Menu

Fourteen different plots are available from the Data Type Drop-Down List Box in the Options Dialog Box. These are as follows:

1. -Z” - Z’ (Nyquist plot)

2. -Y” - Y’

3. Log Z - Log(ω) (Bode plot)

4. Log Y - Log(ω)
5. θ - Log(ω) (Bode plot)
6. -Z” & Z’ - Log(ω)
7. -ωZ” - ωZ’
8. -ωY” - ωY’
9. -Z“/ω - Z’/ω’
10. -Y“/ω - Y’/ω
11. Z’ - ωZ”
12. Z’ - Z“/ω
13. -Z” & Z’ - 1/Sqrt(ω)
14. Cot(θ) - Sqrt(ω)

Section 10. PRACTICAL CONSIDERATIONS

It is highly advisable to run all experiments in the Faraday cage provided with the A.C. Impedance Module to avoid external electronic interferences.

The data analysis procedure assumes the response is linear with the input AC waveform and, generally, for this to be true the A.C. amplitude is relatively small; i.e., a few millivolts. There are exceptions but the key point is the linearity of the output with respect to the input.

The analysis is not valid unless the system is stable thus the electrode at the test potential is assumed to be at an equilibrium or steady state; at least not changing over the time of the experiment.

Impedance data can be difficult to interpret. Some caution and experience is necessary to reach meaningful conclusions.

Be careful when doing subtractions of RC equivalent networks. The electrochemical system may not be acting like electronic components.

The following are some considerations when applying two decades of frequency at one time versus a single decade. (FREQUENCY RANGE query is under Specific Parameters.)

Two decades at a time can only be done with frequencies less than 0.1 Hz. This is because, applying the lower frequency decades require the longest times and so doing two at once can save some time but at the considerable expense of S/N. For example, just doing one cycle where the base, lowest frequency is 1.0 millihertz, the minimum time required is 1000 seconds (16.7 minutes). If multiple cycles are requested to improve S/N, then multiples of this time will be needed. Then the next frequency decade will be run. Depending on whether or not the specifications were one or two decades, the next base frequency will be 10 mHz or 100 mHz. If 10 mHz, one cycle requires minimally 100 seconds and more cycles require multiples of this etc.

Also, another point worth noting is the current response is frequency dependent and if two decades are covered at once then the response at the lowest frequency will be, in the worst case, 100 times less than the highest frequency. The low frequency response could be limited by the digital resolution of the instrument, i.e. added noise.

A third point is many more frequencies are being summed at the same time thus the absolute amplitude at some times could be quite large if two decades are done. This is relative to the ideal case where a few millivolts are being applied and the system is assumed to be in a equilibrium state and responding in a linear fashion. An electrochemical system is not linear beyond a few millivolts of the equilibrium potential.

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