TechnicalNOTE

Impact on EIS using the Reference 600 / 3000 with an ECM8 Multiplexer

Purpose of This Note

This technical note discusses the Electrochemical Impedance Spectroscopy (EIS) performance of Gamry's multiplexed EIS systems. Two basic impedance experiments show the limitations and the changes in EIS performance when Gamry's Electrochemical Multiplexer ECM8 is connected to a potentiostat.

It further discusses the impacts of these limitations on research in the areas of coatings and energy storage devices.

Introduction

We assume the reader of this note knows the basics of EIS. If this is not the case or the user wants to brush up on EIS, we recommend the Application Notes section on Gamry's web site: www.gamry.com. Theoretical concepts of EIS will not be discussed in this note.

The ECM8 Multiplexer is a powerful measurement device. It is equipped with eight independent channels which enable higher throughput of electrochemical measurements. Front and back side of the ECM8 are shown in Figure 1.

Figure 1 - Front and back view of the ECM8 Multiplexer.

The ECM8 can be connected to all Gamry potentiostats or other 3rd party devices. One cell at a time can be accessed by the system potentiostat and electrochemical measurements can be performed.

A special characteristic of the ECM8 Multiplexer is the local potentiostat. Each of the eight channels has its own local potentiostat that allows potential control of inactive cells between readings.

The ECM8 Multiplexer allows the use of all electrochemical applications that are included in Gamry's Framework.

One commonly used technique is the Electrochemical Impedance Spectroscopy. This very powerful technique is applicable for investigations of different applications:

- Corrosion
- Paints and Coatings
- Batteries and Electrochemical Capacitors
- Fuel cells

The ECM8 Multiplexer, combined with a potentiostat, allows sequential measuring of EIS spectra. The measurement setup has to be built up just once and long-term tests can run without human intervention, reducing labor requirements and instrumentation costs.

Basically, EIS is non-destructive to the investigated system. This allows combination with other techniques and the investigation of changes in a system with respect to time. Further, EIS allows the user to model the underlying system and the reaction mechanism. This contributes to a better understanding of the process and can lead to more precise results.

To have confidence in EIS results it is important for the user to know the limitations and specifications of the EIS system that was used for investigations. For this purpose, two basic EIS tests (Open Lead and Shorted Lead) were performed to obtain the EIS system's limitations.

Measurements were done using Gamry's Reference 600 and Reference 3000 as stand-alone units. Changes in EIS limitations also were measured when an ECM8 Multiplexer was connected to each potentiostat.

Experimental

For measurements with an ECM8 Multiplexer, a Gamry Instruments shielded cable (P/N 985-00080) was used to connect the potentiostat with the ECM8.

An additional interface cable (P/N 985-00108) between the shielded cable and potentiostat was needed to connect the ECM8 to a Reference 3000.

Communication between computer and Multiplexer was achieved by a RS232 cable.

EIS tests were performed only on one channel; hence one 1.5 m long cell cable (P/N 985-00038) was connected to one channel port at the rear side of the ECM8. The seven inactive channels were not connected. The local potentiostats of inactive channels were turned on with their voltages set to 0 V.

Two different tests were performed to check the limitations of Gamry's EIS systems with and without the ECM8 Multiplexer. The next sections describe the dummy cell connections and the EIS measurements.

Note that all measured values strongly depend on the quality of the setup and devices used. Therefore, this technical note can only give approximate values.

Open Lead test

The Open Lead test gives the user information about the maximum measurable impedance and minimum measurable capacitance of a system.

The setup for this test simulates infinite impedance with a large air-gap between the cell leads. The two Working leads (green and blue) are connected and placed in a Faraday cage. The Reference (white) and both Counter leads (red and orange) are connected together and left outside of the Faraday cage. The Faraday cage is grounded to the potentiostat's ground lead (black).

The cell cable of an ECM8 comes up with two black grounding terminals – earth ground (shorter) and floating ground (longer). When using a Faraday cage, the floating ground must be connected, and the earth ground should be connected.

If 3rd party potentiostats are used, Reference and Counter leads should be placed within the Faraday cage. Strong noise could affect the measurement signal. The minimum distance between Working and Reference/Counter leads should be at least 20 cm.

The Open Lead test involves a potentiostatic EIS experiment. Gamry's EIS300 software includes a script called ***Multiplexed Potentiostatic EIS***. This script is similar to the standard potentiostatic EIS experiment but includes individual parameters for each ECM8 channel.

All spectra were recorded in the *Low Noise* mode to obtain higher accuracy.

Shorted Lead test

The Shorted Lead test yields the lowest measurable impedance of a system. A shorted configuration of the electrodes simulates the ideal of zero impedance.

The test setup uses a 4-electrode configuration where current carrying and sense leads are carefully separated. Resistances of metal connections can falsify the experiment and cannot be ignored. A copper block with separate connections is used as dummy cell.

Figure 2 shows the Shorted Lead dummy cell and the connections of the four terminals.

Figure 2 – Shorted Lead dummy cell and cell cable connections. Working (green), Counter (red), Working sense (blue), and Reference (white).

For the setup, Counter (red) and Working lead (green) are connected by a banana jack to the copper block. Both leads are twisted together to minimize the radiated external field that can interfere with the low-impedance test. Reference (white) and Working sense lead (blue) are also twisted together and connected to a holding pin at the other side of the copper block.

The whole test assembly is placed within a Faraday cage that is grounded to the potentiostat's ground. The Counter sense lead (orange) also can be connected to the Faraday cage. As before, when using the ECM8, both black leads are linked to the Faraday cage.

The Shorted Lead spectrum must be measured using a galvanostatic EIS experiment. Gamry's ***Sequence Wizard*** enables the possibility to perform flexible procedures with the ECM8 where individual channels can be selected.

The EIS spectra were recorded in the *Low Noise* mode to obtain higher accuracy.

Results and Discussion

Open Lead tests on the Reference 600

Figure 3 shows the Bode plots of the Open Lead tests with a Reference 600 as stand-alone unit (blue) and connected with an ECM8 (red) respectively.

The impedance spectra were recorded from 1 MHz and 100 kHz respectively to 1 mHz. Zero DC voltage with an AC voltage of 50 mV_{rms} was applied.

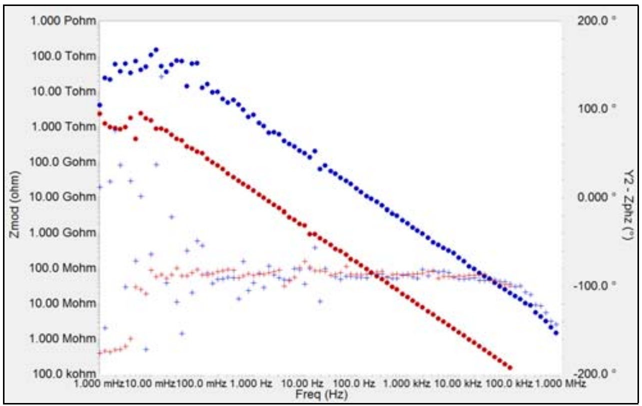

Figure 3 – Open Lead plot of a single Reference 600 (blue) and connected with the ECM8 (red). (●) magnitude, (+) phase.

The spectrum of the Reference 600 connected with the ECM8 is shifted toward the bottom left corner of the plot.

Over a wide frequency range both EIS systems show capacitive behavior. Impedance increases linearly with decreasing frequency down to about 100 mHz and 10 mHz respectively. The phase angle is about -90°.

At lower frequencies the magnitude flattens to resistive behavior. This region yields the maximum impedance of the EIS system.

The single Reference 600 has its highest impedance in a region between 10 TΩ and 100 TΩ (10^{13}–10^{14} Ω). This value exceeds by far the low-frequency Open Lead impedance of most EIS systems. Maximum impedance is dominated by the ECM8 when the Multiplexer is connected. The impedance is reduced by about two decades and varies between 0.5 TΩ and 5 TΩ.

The whole Open Lead spectrum models as resistor parallel to a capacitor (RC-model). The fit yields for the single Reference 600 a capacitance of about 90 fF. This is the smallest measurable capacitance of this system. The ECM8 Multiplexer limits this value to 10.9 pF which is about two decades higher.

The resistance values for the low-frequency range of the RC-model are less meaningful. For completeness, the fit yields -3.5 TΩ for the single Reference 600, with the ECM8 this value is about -190 GΩ.

Note the negative resistances of this fit. A perfect negative resistance would have a +180° phase shift. Noise in the signal causes noise in the phase. As a result, Open Lead phase often varies between plus and minus 180°.

Shorted Lead tests on the Reference 600

Figure 4 shows Shorted Lead Bode plots using a single Reference 600 (blue) and the same unit connected to an ECM8 (red).

The spectra were recorded from 50 kHz to 10 mHz. The applied AC current was 300 mA_{rms} with zero DC current.

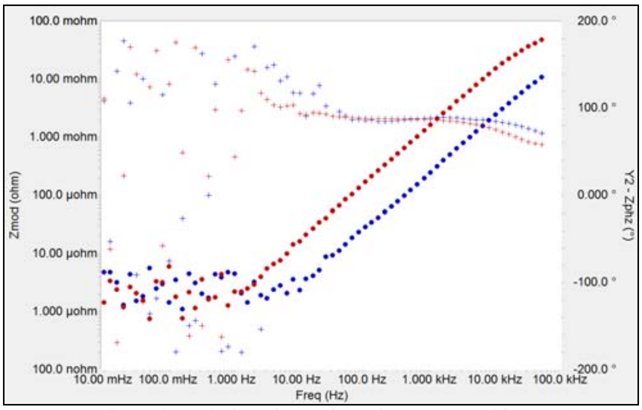

Figure 4 – Shorted Lead plot of a single Reference 600 (blue) and connected with the ECM8 (red). (●) magnitude, (+) phase.

The spectrum of the EIS system with the ECM8 is shifted toward the left side of the plot.

In contrast to the Open Lead test, Shorted Lead spectra show inductive behavior at higher frequencies. The phase is about +90°. Impedance decreases linearly with decreasing frequency.

Below 10 Hz and 1 Hz respectively both spectra flatten and show resistive behavior. This region gives the minimum impedance of the system. For both EIS systems this value is in the region between 1 μΩ and 10 μΩ. This region is completely dominated by the Reference 600.

The total Shorted Lead spectrum models as resistor in series with an inductor (RL-model). The fit yields an inductance of about 40 nH in the spectrum for no Multiplexer. When the ECM8 is connected the inductance increases to about 250 nH.

The Shorted Lead test for a single Reference 600 was done with a standard 60 cm cell cable. Significantly lower inductances can be achieved by using Gamry's special ***Low-Impedance cell cable*** (P/N 990-00239).

The resistance value of the RL-model is about -935 nΩ for the single Reference 600, connected with the ECM8 the resistance is about -430 nΩ.

Note again the negative resistances. When measuring very low impedances, the applied signal can be much larger than the sensed signal. Signal leakage leads to positive or negative resistances. In this case, phase varies between plus and minus 180°.

Open Lead tests on the Reference 3000

Before starting measurements with the Reference 3000, its voltage setting was changed to ***High Voltage, Low Current mode***. That limits the output current to ±1.5 A. This step is recommended to avoid damaging the relays of the ECM8 Multiplexer whose maximum rated current is 2 A.

Figure 5 shows the Open Lead Bode diagrams of the Reference 3000 alone (blue) and with the ECM8 (red). The potentiostatic EIS spectrum was recorded from 1 MHz and 100 kHz respectively to 1 mHz. Zero DC voltage with an AC voltage of 50 mV_{rms} was applied.

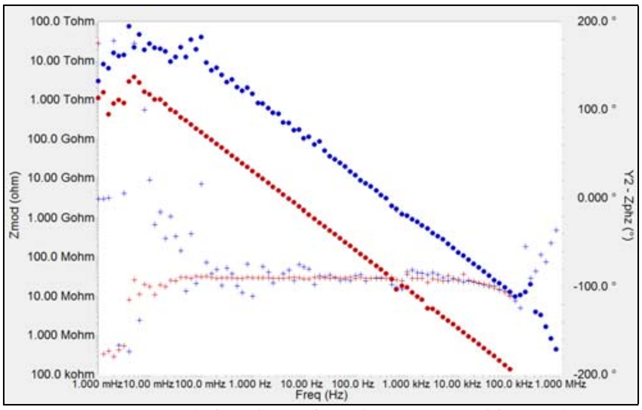

Figure 5 – Open Lead plot of a single Reference 3000 (blue) and connected with the ECM8 (red). (●) magnitude, (+) phase.

EIS performance is reduced when the ECM8 Multiplexer is connected to the Reference 3000. The spectrum is shifted toward the bottom left corner of the Bode plot.

The maximum impedance in the low-frequency range of the single Reference 3000 is in the region from 5 TΩ to 50 TΩ. With the ECM8 the region is reduced by about one decade and varies from 0.5 TΩ to 5 TΩ.

The whole Open Lead spectrum models as a parallel RC-circuit. For the single Reference 3000 the lowest measurable capacitance is about 135 fF. Connected with the ECM8, the EIS system's capacitance increases to 11.0 pF. This value is similar to the result of the Open Lead measurement with the Reference 600 and ECM8.

The resistance of the RC-model is about 6 TΩ for the Reference 3000, with the ECM8 it fits to about -1 TΩ. Note that resistance values can also be negative.

Comparison of these Open Lead measurements with those for the Reference 600 (see Figure 3) shows that both highest impedance and lowest capacitance are similar when the ECM8 is connected. That means the ECM8 is the limiting factor for these values. Hence it makes no difference at high impedance measurements which potentiostat is used when an ECM8 Multiplexer is connected.

Shorted Lead tests on the Reference 3000

Figure 6 shows the Bode plots for the corresponding Shorted Lead tests with the same Reference 3000 alone (blue) and connected with the ECM8 (red).

The galvanostatic EIS measurements were done from 100 kHz to 10 mHz with an AC current of 1 A_{rms} and zero DC current.

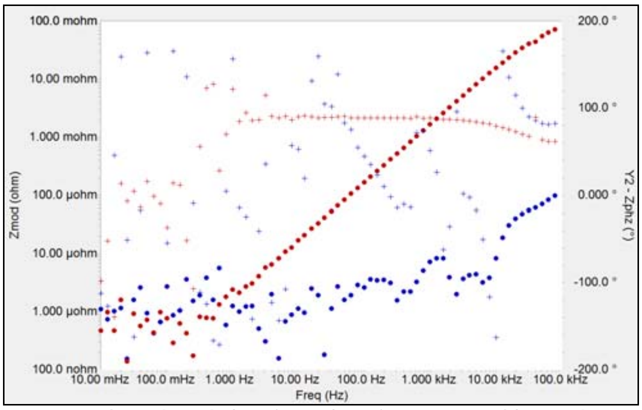

Figure 6 – Shorted Lead plot of a single Reference 3000 (blue) and connected with the ECM8 (red). (●) magnitude, (+) phase.

The Shorted Lead plot of the single Reference 3000 is very noisy. While the spectrum is more or less shaped like that of a series RL-model, standard fitting algorithms didn't fit these data well. Hence appropriate model values were visually estimated from the plot.

In both curves, the lowest measurable impedance is in the region between 0.1 µΩ and 10 µΩ. For the single Reference 3000 this region reaches up to 10 kHz. With the ECM8 the region is limited to a frequency range below 1 Hz. The lowest measurable impedance is dominated by the Reference 3000.

Assuming a serial RL-model, the Shorted Lead inductance for a single Reference 3000 was estimated at

250 pH. With the ECM8, the fit to the RL-model yields about 250 nH which is three decades higher. This value corresponds with the Shorted Lead measurements with the Reference 600 (Figure 4). Hence the Shorted Lead inductance is limited by the ECM8.

For completeness, the estimated resistance value of the RL-model for the Reference 3000 is 100 nΩ. With the ECM8 this value is about 140 nΩ. Both resistances are positive in this fit, though noise in the sensed signal could lead to negative values. The effect of noise also can be seen in the plus and minus 180° phase variance.

Summary

In the Open Lead measurements, while no ECM8 Multiplexer is connected, the Reference 600 shows a slightly lower capacitance than the Reference 3000. The upper impedance limit of the Reference 600 is about twice as large as that of the Reference 3000.

In the Shorted Lead tests without the ECM8, the Reference 3000 exhibits a noisier but much lower inductance. The lowest impedance value is similar to that of the Reference 600, but the frequency range is much wider with the Reference 3000.

When the ECM8 Multiplexer is connected, the regions of lowest capacitance, lowest inductance, and highest impedance are limited by the ECM8. For most users, in these cases it makes no difference which potentiostat is used if the ECM8 is connected.

Only the low-impedance region in Shorted Lead tests is limited by the potentiostat.

Consequences for Practical Applications

Researchers of coatings and energy storage devices work near the extremes of Open Lead and Shorted Lead tests. Barrier coatings involve very low capacitances and high impedances. In contrast, very low impedances are measured in battery and capacitor research.

Coating tests

As mentioned, high impedances and very low capacitances are characteristics of coatings research.

As an example, assume a coated surface with an area of 1 cm^2. The thickness of the coating is about 100 μm and its relative electrical permittivity is 5. The calculated capacitance would be about 45 pF and the impedance at 1 mHz about 3.6 TΩ.

Compared to the Open Lead spectrum with the ECM8, the corresponding Bode plot of this coating would be a straight line parallel to the Open Lead curve and shifted further towards the bottom left corner.

The measured capacitance would be still within the limitation of the ECM8 which is about 11 pF. However, the closer the measured capacitance is to the limit the bigger is the error of the measurement.

At frequencies below 10 mHz the measured impedance would be close to the region where it is limited by the ECM8. Use caution in evaluation especially at low frequencies where impedance can exceed the limits.

To be sure within the limitations, reduce the coating thickness or increase the probe area. If that is not possible, then use only a single potentiostat.

Battery and Electrochemical Capacitor tests

In energy storage research, all series resistive terms are summed up to one single term called "Equivalent Series Resistance" (ESR). Small ESR are required for more efficient batteries and electrochemical capacitors. Hence, measurement of very low impedances and resistances is necessary.

For batteries and electrochemical capacitors, ESR generally is several mΩ and can get to the sub-mΩ region.

Figure 7 shows a magnitude-only Bode plot of galvanostatic EIS experiment of a 650 F EDLC from Nesscap (P/N BCAP0650 P270) (purple) and an 80 Ah Li-Ion battery (green).

The AC current was 1 A_{rms} and 0.5 A_{rms} respectively with zero DC current. The experiment was done from 100 kHz to 10 mHz.

Both plots are compared with Shorted Lead spectra of a single Reference 600 and a Reference 3000 with and without an ECM8 (see also Figure 4 and Figure 6).

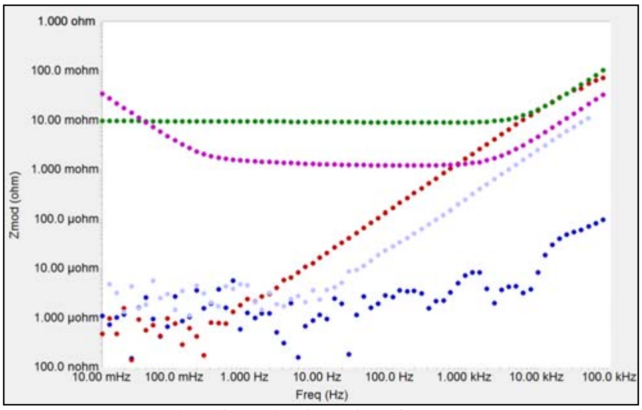

Figure 7 – Magnitude-only Bode plots of a galvanostatic EIS test of an 80 Ah Li-Ion battery (green) and a 650 F EDLC (purple) compared to Shorted Lead spectra of a Reference 3000 without (blue) and with an ECM8 (red) and a single Reference 600 (light blue). (●) magnitude.

A serial RL-model can be used to fit the magnitude of the Li-Ion battery (green curve). The fit yields for the

ESR about 10 mΩ and for the inductance about 210 nH.

The measured inductance is lower than the Shorted Lead inductance when an ECM8 is connected. Hence it would be limited by the ECM8.

At 1 kHz the impedance of the Li-Ion battery is about 9 mΩ. This is higher than the values of the Shorted Lead spectra – with and without ECM8 – and within the limitations.

For frequencies below 10 kHz the ECM8 can be connected to any potentiostat without further restrictions. In this region, the measured impedance is higher than the lowest measurable. Above 10 kHz the spectrum would be limited when an ECM8 is connected.

The Bode diagram of the 650 F EDLC (purple curve) was fitted with a Bisquert Open model in series with an inductor. The fit yields for the ESR about 1 mΩ and for the inductance 70 nH. As before, the measured inductance would be limited by the ECM8.

For frequencies below 1 kHz the capacitor's Bode plot is within the limitations of all Shorted Lead spectra. Above 1 kHz the spectrum exceeds the limitations when an ECM8 is connected.

In summary, for low-impedance measurements the ECM8 can be used at low frequencies without any restrictions. At higher frequencies – depending on the investigated system – the ECM8 would limit the measurement. For these regions it is recommended to use only a single potentiostat without the ECM8.

C3 Prozess- und Analysentechnik GmbH
Peter-Henlein-Str. 20
85540 Haar b. München

Tel: 089/45600670
FAX: 089/45600680

info@c3-analysentechnik.de
www.c3-analysentechnik.de

www.gamry.com