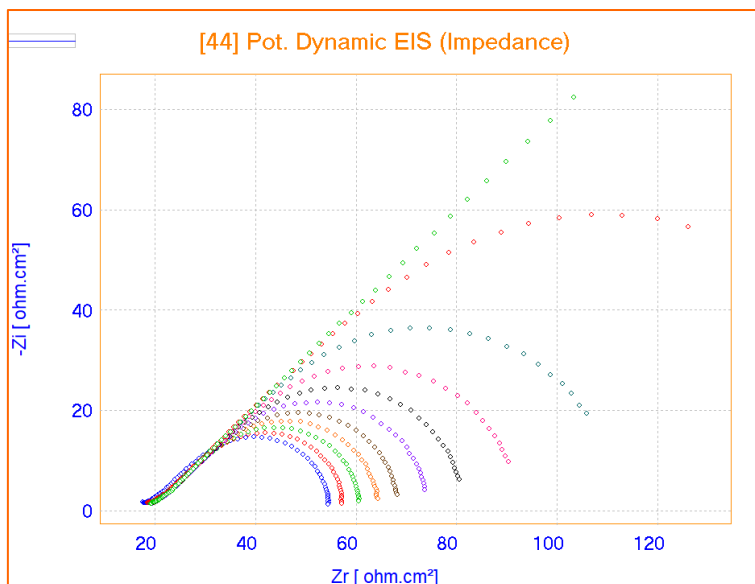




General Electrochemistry AP-GE09

Pot. Dynamic EIS



This Application Note describes how to use the Pot. Dynamic EIS method, combined with different RDE rotation speed.



Introduction

Electrochemical Impedance Spectroscopy (EIS) is used to investigate electrochemical processes through extracting electrical circle. In fact, an electrochemical cell will be simulated to an electrical circuit. A Pot. Dynamic EIS experiment will generate an individual electrochemical impedance spectra obtained at a given DC potential. This spectra reports the impedances measured at various frequencies with a superimposed AC sinus wave.

Main application of EIS method is the study of surfaces, batteries, corrosion, photovoltaic systems and some life science researches. It is based on introducing a perturbation into the system being studied by means of a sine wave current or small amplitude potential.

The result of the impedance test helps the user to obtain an electrical version of the electrochemical cell by which many qualitative data could be extracted through Nyquist plot.

WHY EIS: Impedance method is an **in-situ technique and non-destructive**. The technique is most sensitive when the defect is close to the surface and the base structure is relatively stiff.

A Nyquist plot is an alternative way of representing the frequency response characteristics. It uses Cartesian coordinates in two dimensions whose ordinate represents the imaginary axis and abscissa represents the real axis as resistance.

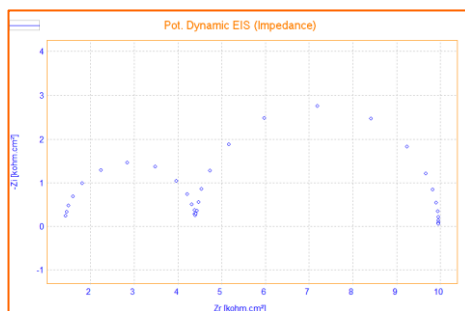


Figure 1: Double loop Nyquist plot

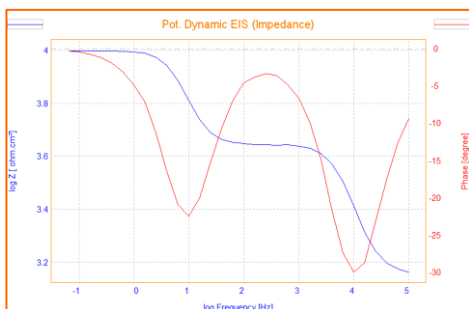


Figure 1: Bode plot

Bode is also another way to plot an impedance spectrum. It's two plots in one. The advantage of this is that all information is clearly visible. For instance: a capacitor in parallel to a resistor, is visible in this spectrum as a peak in the phase shift.



Parameters

To perform an EIS test, the DC potential can be set at ± 15 V versus the REF potential or even it can be defined as OCP value (free). With the OrigaStat range, the Electrochemical Impedance spectrum can be recorded from 1 kHz down to 10 μ Hz (extendable to 5 MHz with the OGFEIS module).

The AC sine wave amplitude can be set from 1 mV up to 1,000 mV. Nyquist or Bode diagrams are available as a real-time plot display.

This experiment was performed by OrigaMaster software. The parameters are shown in figure 3.

The EIS method was run 11 times and each time the rotation speed of RDE was increased. First loop is 0, last one is 2,000 rpm.

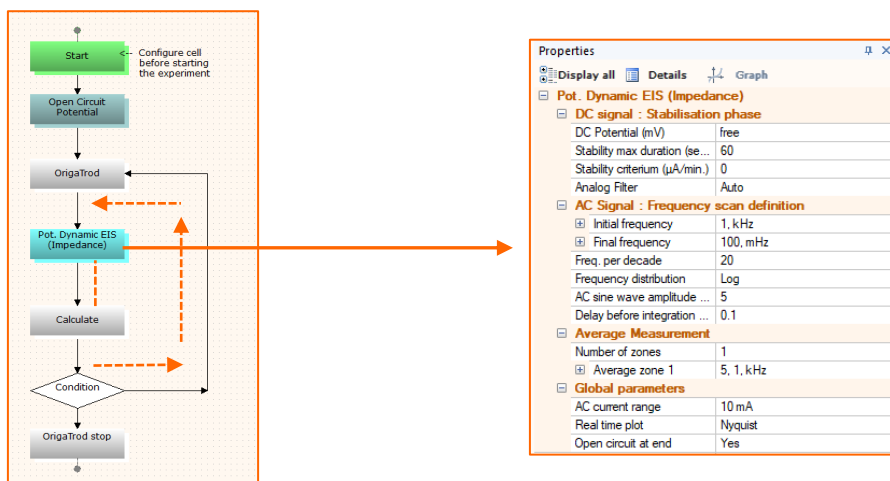


Figure 3: The parameters of impedance test

TIPS: Before sweep the potential, the OCP of working electrode was measured for 4 minutes to have more stable working electrode. It's very important to perform Impedance measurement with a stable working electrode.



HOW TO SET THE PARAMETERS

To get good results, some parameters need to be chosen with care. Indeed, if the parameters are not optimized, the curve could be too noisy and so useless for publications and post-treatment.

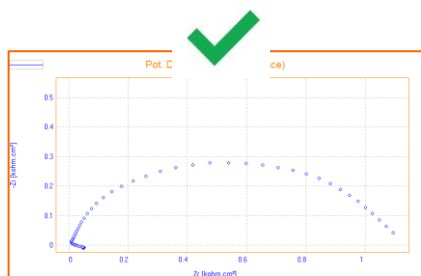


Figure 4: Good curve

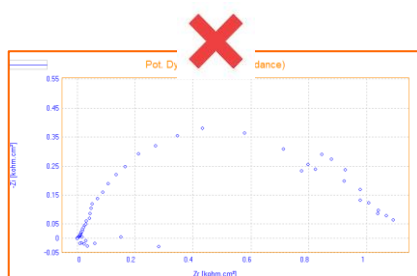


Figure 5: Bad curve, too noisy

Properties	
Display all Details Graph	
Pot. Dynamic EIS (Impedance)	
DC signal : Stabilisation phase	
1	DC Potential (mV) free
	Stability max duration (sec) 60
	Stability criterium (µA/min) 0
	Analog Filter Auto
AC Signal : Frequency scan definition	
	Initial frequency 1, kHz
	Final frequency 100, mHz
	Freq. per decade 20
	Frequency distribution Log
2	AC sine wave amplitude 5
	Delay before integration ... 0.1
Average Measurement	
3	Number of zones 1
	Average zone 1 5, 1, kHz
Global parameters	
4	AC current range 10 mA
	Real time plot Nyquist
	Open circuit at end Yes

Figure 6: Optimized parameters for OGS100

TIPS: Parameters can be optimized to get a smooth curve. But it does not prevent from also optimizing the electrode connections : shielded cables, Faraday cage, and so on.

Most important parameters:

1: Stability max duration

This is the equilibration step. Too often, it's an underestimate parameter, but it's a very crucial one. If the signal is not stable, the results cannot be good. Depending on the sample, we recommend to put between 1 and 10 minutes.

2: AC sine wave amplitude zero to peak

Normally, the AC amplitude is between 5 and 10 mV, but for some samples, it could be increased, up to 50 mV.

3: Average

The number of measurement repetitions performed for each frequency. We recommend to put at least 5 as average. Putting an average upper than 1, impacts the total duration.

In our example:

- Average = 1 = Total duration = 12 minutes
- Average = 5 = Total duration = 32 minutes

4: AC current range

Very crucial parameter. Putting a fixed current range, fitting the current which flows in the cell is the best solution to get optimized results.

In our example:

the best current range is 10mA.



HOW TO REDUCE THE DURATION

During method programming, you can get some data on the experiment, by clicking twice on the method block.

Properties	
Display all	Details
Graph	
Pot. Dynamic EIS (Impedance)	
DC signal : Stabilisation phase	
DC Potential (mV)	free
Stability max duration (se...)	60
Stability criterium (µA/min.)	0
Analog Filter	Auto
AC Signal : Frequency scan definition	
Initial frequency	1, kHz
Final frequency	100, mHz
Freq. per decade	20
Frequency distribution	Log
AC sine wave amplitude ...	5
Delay before integration ...	0.1
Average Measurement	
Number of zones	1
Average zone 1	5, 1, kHz
Global parameters	
AC current range	10 mA
Real time plot	Nyquist
Open circuit at end	Yes

Definition:


The frequency scan is determined within two selectable limits: Initial and Final frequency. The number of frequency values is set by the frequencies per decade value. It sets the number of points of one impedance spectrum.

Reducing the duration of the measurement:

By having less points per spectrum, you get less EIS data, and so the maximum duration is decreased.

TIPS: The equivalent circuit is more trustable with 20 as Freq. per decade.

Figure 7: The parameters of impedance test


OriginaMaster 5	
	Number of points = 81 Stabilisation Max. Duration = 01 min. 00.00 sec. Spectrum Max. Duration = 32 min. 43.00 sec.
<input type="button" value="OK"/>	

Freq. per decade = 20

Average = 5

Number of points = 81

Duration is about 32 minutes


OriginaMaster 5	
	Number of points = 41 Stabilisation Max. Duration = 01 min. 00.00 sec. Spectrum Max. Duration = 17 min. 09.00 sec.
<input type="button" value="OK"/>	

Freq. per decade = 10

Average = 5

Number of points = 41

Duration is about 17 minutes

OriginaMaster 5	
	Number of points = 21 Stabilisation Max. Duration = 01 min. 00.00 sec. Spectrum Max. Duration = 09 min. 24.00 sec.
<input type="button" value="OK"/>	

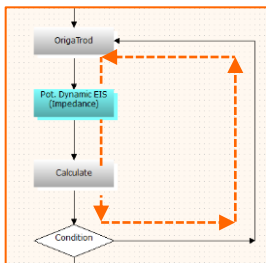
Freq. per decade = 5

Average = 5

Number of points = 21

Duration is about 9 minutes





TIPS: By using “Calculate”, “Condition” and “Linkable line” tools, we create a manual loop. By this way, the Impedance method can be repeated as many time as needed through a defined cycle. In each cycle the rotation speed of the RDE is different.

TIPS: For more information about creating a manual loop, please read our application note AP-GE08.

Results

An overlay of the 11 EIS curves made from the loop and by different rotation speeds of the RDE are shown in figure 8.

As the X axis is the real resistance per ohm.cm^2 it can be understood that by increasing the speed rotation of RDE, the mass transfer of analyte towards WRK will be increased so the resistance of polarization decreased, and the Nyquist plots become more and more circle like.

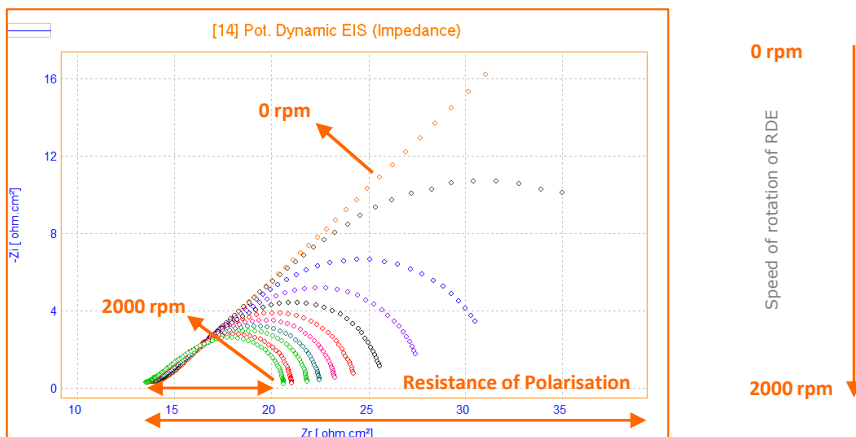


Figure 8: Overlay of 11 Nyquist plots from EIS tests with RDE



EQUIVALENT CIRCUIT TOOL

In the Curve tab, there is an option "Equivalent Circuits" in which there are many circuits as template.

1 Display Nyquist curve and select equivalent circuit

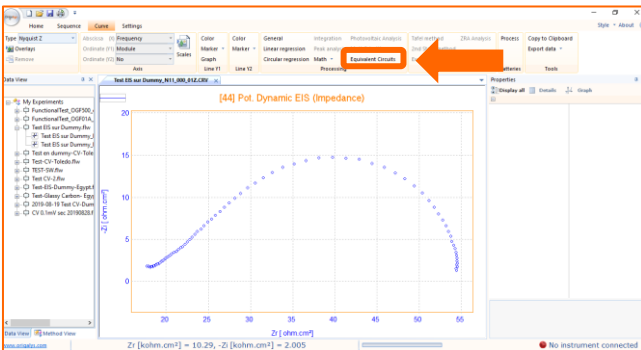


Figure 9: Impedance curve from Pot. Dynamic EIS

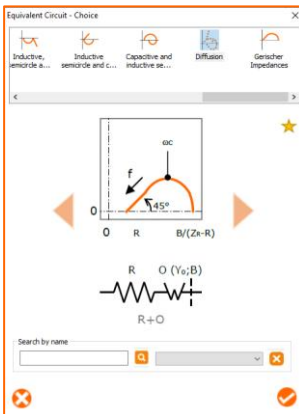
Open the EIS curve

To enable the equivalent circuit option, you need to display an Impedance curve, from Pot. Dynamic EIS and Gal. Dynamic EIS.

Select the option

Click on Equivalent circuit, from Curve Tab, to enter into the option

2 Choose the circuit from the list



Select the category

Find the circuit fitting the shape of your curve in the list, from 14 categories for more than 80 circuits: Capacitive straight lines, inductive straight lines, Capacitive semicircle, Capacitive elliptic, Inductive semicircle, Diffusion, Gerischer, and so on.

Select the circuit

Once inside the category, select the most similar shape to your own curve.

In our example, we have selected Warburg circuit: R+O

Then, press the  to move on.

Figure 10: Capacitive semicircle category



EQUIVALENT CIRCUIT TOOL

3

Fitting your curve

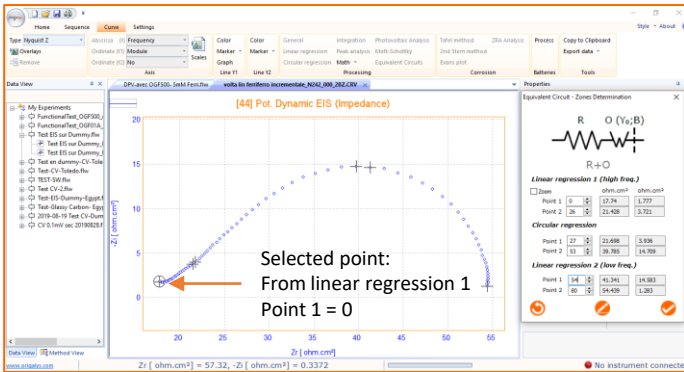


Figure 11: Equivalent circuit, zone determination

Select the zone

To fit your curve, you need to select two points for each regression: point 1 and point 2.

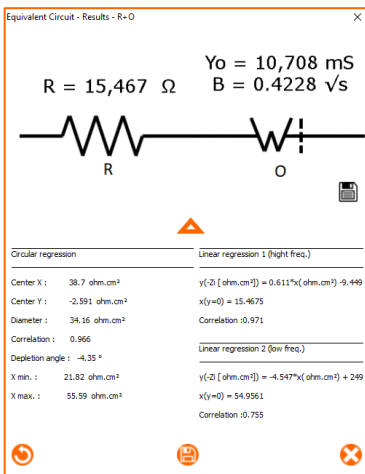
On the Zones determination window, click on the point value, the software put a circle on the point in the graph.

Then, press to visualize the fitting.

If the result suits you, press to move on.

4

Final results and data



See the results

Once validated, you get the final results and the values of your circuit elements:

- $R = 15.467 \Omega$
- $Y_0 = 10.708 \text{ mS}$
- $B = 0.4228 \sqrt{s}$

Other data are also available by clicking on .

Save the results

The data can be saved as a text file, by clicking on .

TIPS: Click on return to come back to the zone determination.

Figure 12: Data of the circuit



CONCLUSION: Electrochemical Impedance Spectroscopy (EIS) is one of the most complex techniques in electrochemical research. But, it's quite popular because it makes many changes visible that other techniques don't see. Another common technique in EIS is equivalent circuit. Each electrical component represents a part of the electrochemical system. The equivalent circuit should create the same impedance spectrum as the real electrochemical system.

Instrument and Electrodes



Figure 13: OrigaStat OGS100

Electrode setup

Reference Electrode (REF)	Calomel Type: OGR003
Counter Electrode (AUX)	Platinum wire Ø1mm Type: OGV005
Working Electrode (WRK)	Platinum Ø5mm Type: EMEDPTD5 + OrigaTrod
Electrolyte	Ferri/Ferrate solution 5 x 10 ⁻² M in KCl
Instrument	OrigaStat OGS100
Software	OrigaMaster



Figure 14: Electrochemical cell

REF
Calomel



AUX
Platinum wire Ø1 mm



WRK
OrigaTrod +
Platinum Ø5 mm



OrigaLys ElectroChem SAS

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