Equivalent circuit fitting with non-linear elements

Abstract

A novel tool for EIS data analysis was developed for the study of nonlinear impedances, as an extension of the equivalent circuit analysis. The higher order impedances of an electrochemical process can be determined by using the combined 1st, 2nd, and 3rd harmonic responses. This method can be executed with the same ease as the classical equivalent circuit analysis. It can be applied on most Electrochemical Equivalent circuits, accounting for series and parallel elements in a rigorous manner, such as in the Randles circuit, on the full frequency range.

Electrochemical objects generally have a non-linear IV relation, therefore the amplitude must be kept small for the classical EIS linear analysis to be valid. Although non-linear EIS has been applied on several occasions, its use has been limited due to the complexity of the analysis. This is especially true if other equivalent circuit elements need to be included, such as series resistors and parallel capacitors, as the rigorous analysis is a laborious exercise. That job is made easy by the application of this tool.

There are several advantages of the non-linear analysis. Higher amplitudes may be applied without causing measurement artefacts, resulting in impedance results with a better signal/noise ratio. Also, extra information is obtained from the 2nd and 3rd order impedance derivatives. For Butler-Volmer type reactions, these can be used to determine Tafel slopes and rate constants. For semiconductors and batteries, higher orders offer great potential due to their higher sensitivity.

1. Introduction

The higher orders offer a potential promise for more information. Historically, going from 0th-order (DC) techniques to 1st-order (impedance) meant more measurable parameters[1-4]. Likewise, extending our scope to the higher orders could lead to a comparable extension of descriptive properties.

Real systems in the physical world typically exhibit non-linear electrical relations. Their response is usually not directly proportional to the perturbation. Often, nature exhibits exponential and to-the-power relations. In DC techniques this is well known, and its data is analyzed according to non-linear models. However, in conventional impedance techniques, linearity is assumed, otherwise analysis would become too complex; one assumes that the response is directly proportional to the applied amplitude, and the response normalized to an "amplitude independent impedance".

The assumption of linearity, though formally wrong, can nevertheless be applied in practice when we are using very low amplitudes. At low amplitudes, the higher power responses are small and can be neglected, so the system behaves as if it were linear. The question "which amplitude is small enough", cannot be answered without knowledge about the system to be tested. Often a practical limit of 10mV is advocated. However, there is no guarantee that this is low enough for each system. On the other hand, it may be too conservative for other systems that could benefit from the better measurement accuracy at higher amplitudes.

In potentiostatic impedance spectroscopy, one applies a voltage sinewave with a base frequency, and measures the current response at that same frequency. If the system does not exhibit non-linearity, the current response would be only on that frequency. However, when nonlinearity comes into play, the system will respond with currents on more frequencies.

order	**Amp scaling**	**DC**	**1Hz**	**2Hz**	**3Hz**	**4Hz**	**5Hz**	**6Hz**	**Etc.**
0	1	X							
1	A		X						
2	A^2	X		X					
3	A^3		X		X				
4	A^4	X		X		X			
5	A^5		X		X		X		
6	A^6	X		X		X		X	
7	A^7		X		X		X		X
Etc.									

Figure 1: Response on a 1Hz sinewave perturbation, for a non-linear system

In Figure 1, the table shows the relation with "Orders" and "Harmonics". The 1st order response results in a single harmonic at the base frequency that scales with the amplitude (which is the one we target in conventional impedance spectroscopy). The 2nd order results in a DC offset and an harmonic at 2x the base frequency and scales quadratically with the amplitude, etc. It is important to see that all the higher odd orders (3, 5. ..) will also create a 1st harmonic response, and thus introduce impedance measurement errors in conventional 1st order measurements, see Figure 2.

Also, Figure 1 illustrates the difference between "**order and harmonic**". When we experience 3rd order behavior, we are not only looking at the 3rd harmonic, but also to the 1st. Therefore, these two terms should clearly be distinguished in formulation.

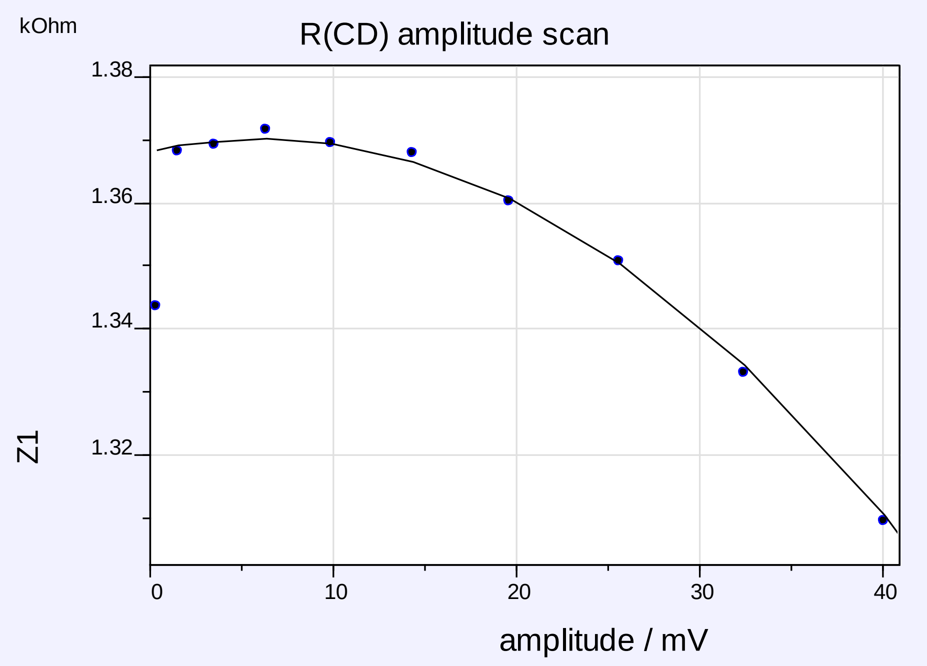


Figure 2: Impedance measurement result, at varied amplitude. The higher odd orders (mostly 3rd), will contaminate the 1st harmonic, resulting in errors at higher amplitudes.

In the practice of conventional impedance measurements, we would like to use as large an amplitude as possible to get the best measurement accuracy, but still avoiding non-linearity errors. Several verification tests have been proposed:

- Visual inspection of the E/I time graphs: The human eye can detect deviations from the pure sine shape. It is often used as first check, but it is not sensitive enough to rule out smaller deviations, and it is subjective.
- Kramers Kronig test: This is a mathematical modelistic calculation from a complete frequency scan. Unfortunately, it is rather unsensitive to nonlinearities, and the data could already be seriously wrong before it fails [5-7].
- Total Harmonic Distortion THD: One calculates the sum of all the harmonics, relative to the base frequency. This has the drawback that it also sums over the even harmonics, which do not cause errors, and data would be disqualified too early. Moreover, it is difficult to define a quantitative threshold above which data should be rejected.
- Amplitude variation: Repeat the experiment at a different amplitude, until the result becomes "amplitude independent". This appears most reliable but takes more time.

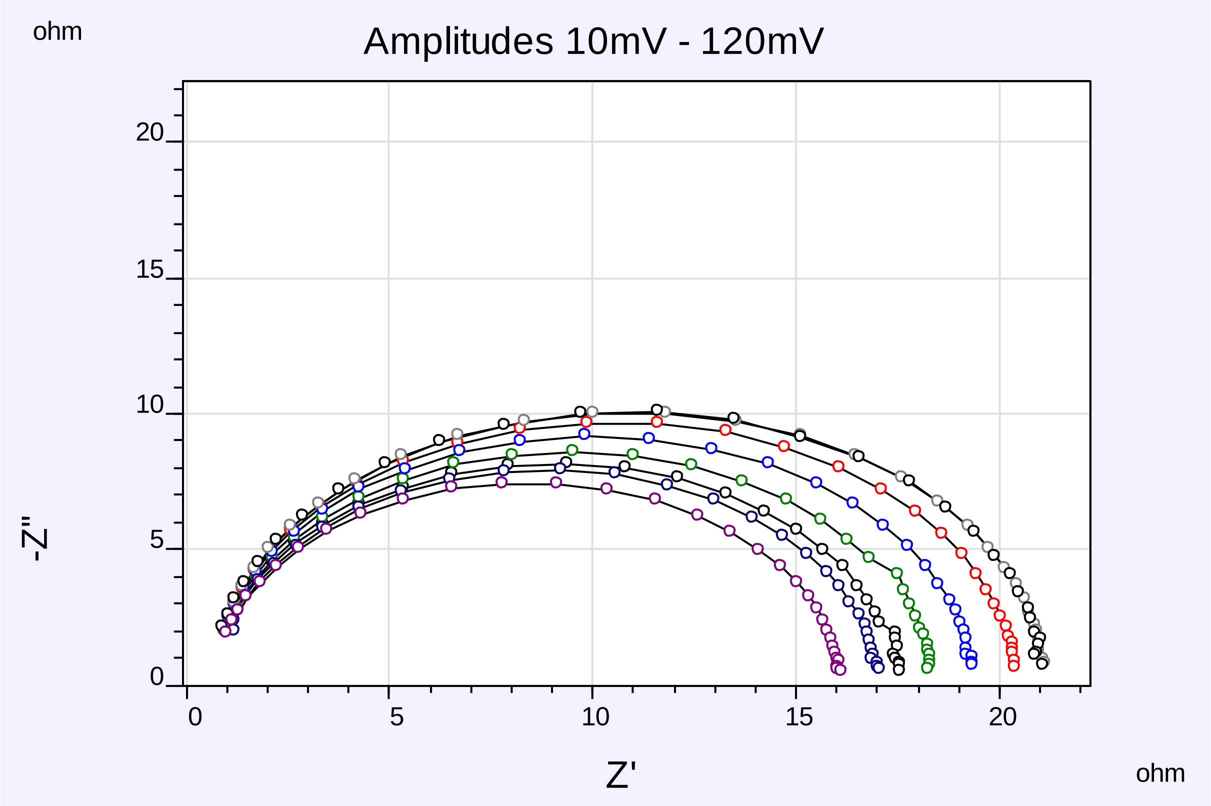


Figure 3: Decreasing Nyquist circle radius at increasing amplitude. Symbols are experimental points, lines are fitting results. All these fit perfectly to the (1st order) equivalent circuit. Therefore, a good quality of fit cannot be used as criterium to rule out linearity errors.

In conventional impedance spectroscopy, when we detect non-linear phenomena in our data, we have little choice but to discard that data, and try again at a lower amplitude, see Figure 3.

2. Deriving information by measuring non-linear responses

2a Potential benefits of non-linear data

Instead of seeing non-linearity as nuisance that must be avoided, one could also try to get useful information from such data. The higher orders tend to be more sensitive to the electrochemical phenomena that we are interested in: Ohmic resistance and double layer capacitances usually do not have much response above the 1st order, so at higher orders, we will see more sensitivity to reaction-kinetics and other surface processes.

When we are collecting higher harmonic data, we extend the amount of dataresults that can be subjected to study. In principle, each extra harmonic will yield an extra set of Bode/Nyquist plots. The availability of the extra plots could discriminate between competing models that could not be discerned from conventional impedance data.

Examples where non-linear analysis is beneficial:

- In electrode kinetics and corrosion, one needs to assume a value for the Tafel slopes to obtain rate constants from EIS data. Using 3rd order data-analysis will remove the need for assumptions, as the rate constants will follow directly from the result.
- Low amplitude techniques may not produce enough accuracy due to a bad signal/noise ratio. A multi-order analysis allows the use of higher amplitudes, without introducing errors.
- When using galvanostatic techniques, we have no control over the voltage, which is the actual driving force causing non-linearities. It is therefore possible to inadvertently get into a non-linear regime. Having the multi-order result available will avoid/detect such errors.
- Batteries and semi-conductors (solar cells) have rather stable first order impedance results. For detecting small changes early, the more pronounced featured results from the higher orders will be more sensitive.

2b Practical analysis

The order refers to the order/power of the differential equation. For example, a 2nd order would correspond to the 2nd derivative of the Potential/Current relation, etc. Also, the response magnitude scales with the amplitude to the power of that order, see Figure 1.

To calculate physical parameters from data, we need to write out the differential equations, and model that to the experimental data. The data would be the impedance data with the list of measured harmonics.

In the 1st order technique (conventional impedance EIS) we have a convenient trick. We can transform our time-domain-data to the frequency domain with Laplace (or Fourier) transformation [3]. In the frequency domain, we can do calculations in a convenient manner, and simply build an “equivalent circuit” by adding standard components together. For higher orders, this “trick” ‘does not apply, and we have to revert back to solving the differential equations for each separate case.

A major complication is the impact of series components in the network. When components are in series with each other, the local amplitude is not the voltage that the potentiostat/galvanostat applies on the external electrodes. Suppose you have a pure resistor in series with a non-linear capacitor, the voltage divides over the two, which varies with frequency. So that capacitor will see a larger amplitude at low frequencies than at high frequencies. Any analysis must take this amplitude variation into account, because the “phenomena under test” are not linearly scaling with amplitude (amplitude cannot be divided out). Sometimes in a non-linear data evaluation, the complication of local-amplitude is avoided by neglecting the series components (such as series resistance) [8]. However, that inevitably leads to a narrowing of the application field, as such assumptions are usually unrealistic for practical systems.

Solving the differential equations, and performing the non-linear network analysis is quite time consuming and tedious. It is not expected that many will go that route. Therefore, we developed a tool “IviFit”, that is as convenient as equivalent circuit fitting, and still can analyze the data rigorously. We abstracted the nonlinearities into a novel component, that does all the required math for higher orders and network analysis. The novel component can be fitted, and will yield the numerical results of the order derivatives. Thus, we maintain universal applicability. This means that we can do the higher order analysis, without prior assumptions on the reactionsmechanisms, mass transfer etc. , actually similar as for conventional 1st order impedance analysis.

3. Non-linear equivalent circuit fitting with IviFit

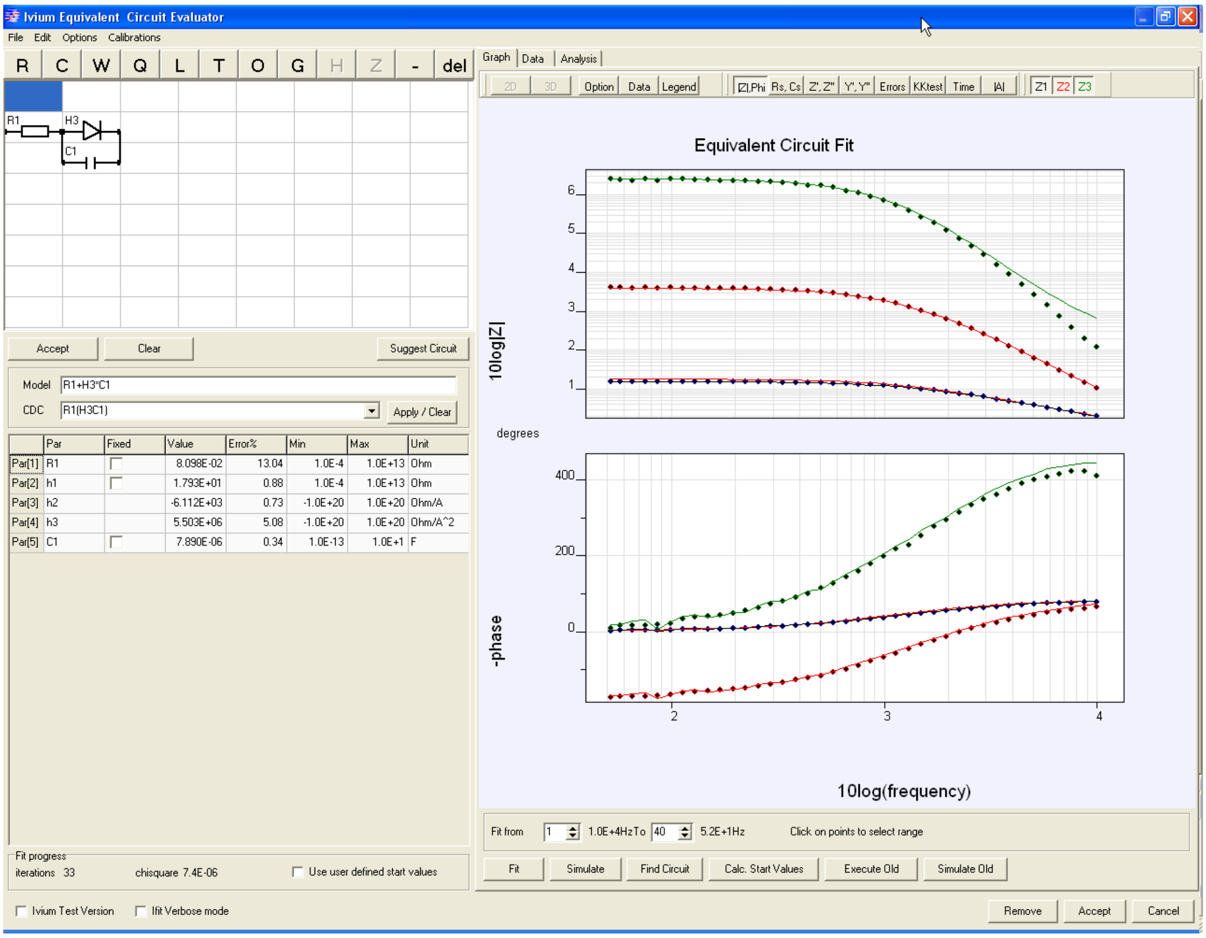
With IviFit, the equivalent circuit can be defined as usual by dropping visual components on a network grid, see Figure 4. The innovation is the introduction of an additional component: H. This component corresponds with a set of derivatives that can apply to any Potential/Current relation. In this manner, the tool is compatible with any electrochemical process of choosing. See Appendix 1, for an example with the Butler-Volmer relation.

The H component can optionally have 2 or 3 orders, selectable in fitting options. These translate to the fit-able parameters h1, h2, and h3. Only one H element can be placed in the network grid, and it cannot be combined with the ladder network Z. At present, the tool is analyzing up to the 3rd order. For most realistic systems, 3 orders are enough to cope accurately with amplitudes up to 150mV.

The fitting can be done as usual. The 3rd order analysis will yield 3 sets of complex plots that are used in the fitting, see Figure 5. The experimental points of the higher order 2 and 3 impedances are calculated indirectly. A proper potentiostat will force a clean 1st harmonic on the cell, so under potentiostatic conditions, there are no experimental 2nd and 3rd harmonic potentials to be measured (for galvanostatic, no higher harmonic currents). We use the relations in Appendix 2, to construct the higher order impedance plots, by relating these to the applied base frequency.

To be complete, we also need to consider the extra DC bias, due to the even orders. The 2nd ,4th ,.. orders will also create a DC response, see Figure 1. Fortunately, their impact can usually be neglected, see appendix 3.

Note that the amplitude is an important property. The plots will sharply change if the experiment would be repeated at another amplitude, or for a system with slightly different resistance. However, the H parameters results h1, h2, and h3 are amplitude independent. Therefore, it is more useful to list and compare the H parameters from different experiments, than it would be to compare raw results.



Model R1+H3*C1

CDC R1(H3C1)

	Par	Fixed	Value	Error%	Min	Max	Unit
Par[1]	R1	☐	8.098E-02	13.04	1.0E-4	1.0E+13	Ohm
Par[2]	h1	☐	1.793E+01	0.88	1.0E-4	1.0E+13	Ohm
Par[3]	h2		-6.112E+03	0.73	-1.0E+20	1.0E+20	Ohm/A
Par[4]	h3		5.503E+06	5.08	-1.0E+20	1.0E+20	Ohm/A^2
Par[5]	C1	☐	7.890E-06	0.34	1.0E-13	1.0E+1	F

Fit progress
iterations 33
chisquare 7.4E-06
☐ Use user defined start values

Fit from 1 1.0E+4Hz To 40 5.2E+1Hz

☐ Ivium Test Version
☐ Ifit Verbose mode

Figure 4: Equivalent Circuit Fitting with a non-linear component (semiconductor). Blue=1st order; red=2nd order; green=3rd order. The symbols are experimental points, whereas the lines are calculated from the fitted model.

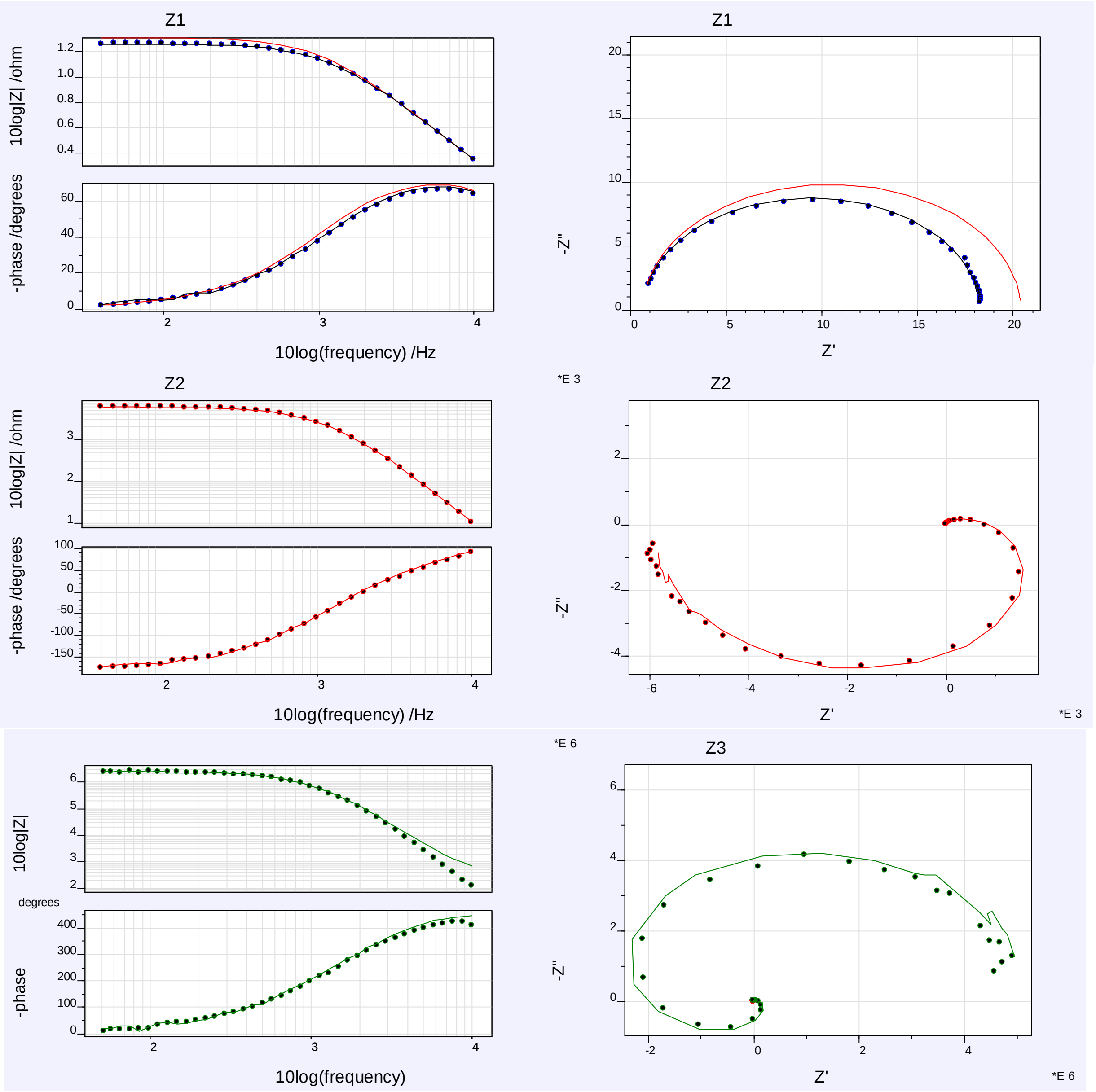


Figure 5: Nyquist plots, corresponding to Figure 4. The extra red line in the Z1 plot is the theoretical 1st order impedance (zero amplitude).

4. Conclusion and discussion

It was demonstrated how the IviFit can be used for non-linear EIS analysis. An equivalent circuit component “H“ was introduced that represents the impedance orders up to the 3rd. The several benefits of this approach are demonstrated:

- Higher amplitudes, up to 150mV, can be used without introducing artefacts, when higher Signal/Noise ratios are required
- IviFit delivers 3 impedance plots, instead of only 1, increasing the amount of information that is obtained from a single experiment.
- IviFit delivers “amplitude independent” higher order dataparameters h1/h2/h3, that allow comparison of data obtained at different experimental circumstances. This is a major point,

because raw data from higher orders cannot be compared sensibly, due to the non-equal scaling of equivalent circuit elements with amplitude. Even if exactly the same amplitude were to be used by the potentiostat, small variations in ohmic resistance or surface area would cause differences in local amplitudes, resulting in major changes in the raw data.

- In corrosion and electrode kinetics, by using a 3rd order analysis, we can obtain the rate constants, without prior assumption of the Tafel slopes.
- For semiconductor (and solarcell) impedance analysis results, we have similar relations from semiconductor theory, and can translate the result to physical meaning.

In cases where the Current/Potential relation has not been fully established yet, such as batteries and fuel cells, the mathematical formulation of the higher order might be difficult. However, the result for h1/h2/h3 can still serve as markers or fingerprints for the state of the system. Moreover, the availability of this data may allow the development & testing of theoretical models, eventually leading to mathematical definition of the derivatives, and therewith giving direct physical meaning to the h1/h2/h3.

The potential advantage of moving to the higher order techniques is the promise of better sensitivity. This was already realized early on [9-10]. It is now well known that the 1st order impedance result is more sensitive than for the 0th order DC technique. Every next higher order derivative is more pronounced and shows more detail. This novel approach could therefore become a powerful addition to the R&D arsenal of tools.

5. References

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Appendix 1 : Example deriving physical meaning from H, using the Butler-Volmer relation

From the Butler-Volmer equation [1]:

$$J = J_0\,(\exp(BaE) - \exp(-BcE))$$

we calculate differentials $Xn = (d^nJ/dE^n)$

$$X1_{E=0} = J_0\,(\,Ba\;+Bc\;)$$

$$X2_{E=0} = J_0\,(\,Ba^2 - Bc^2\,)$$

$$X3_{E=0} = J_0\,(\,Ba^3 + Bc^3\,)$$

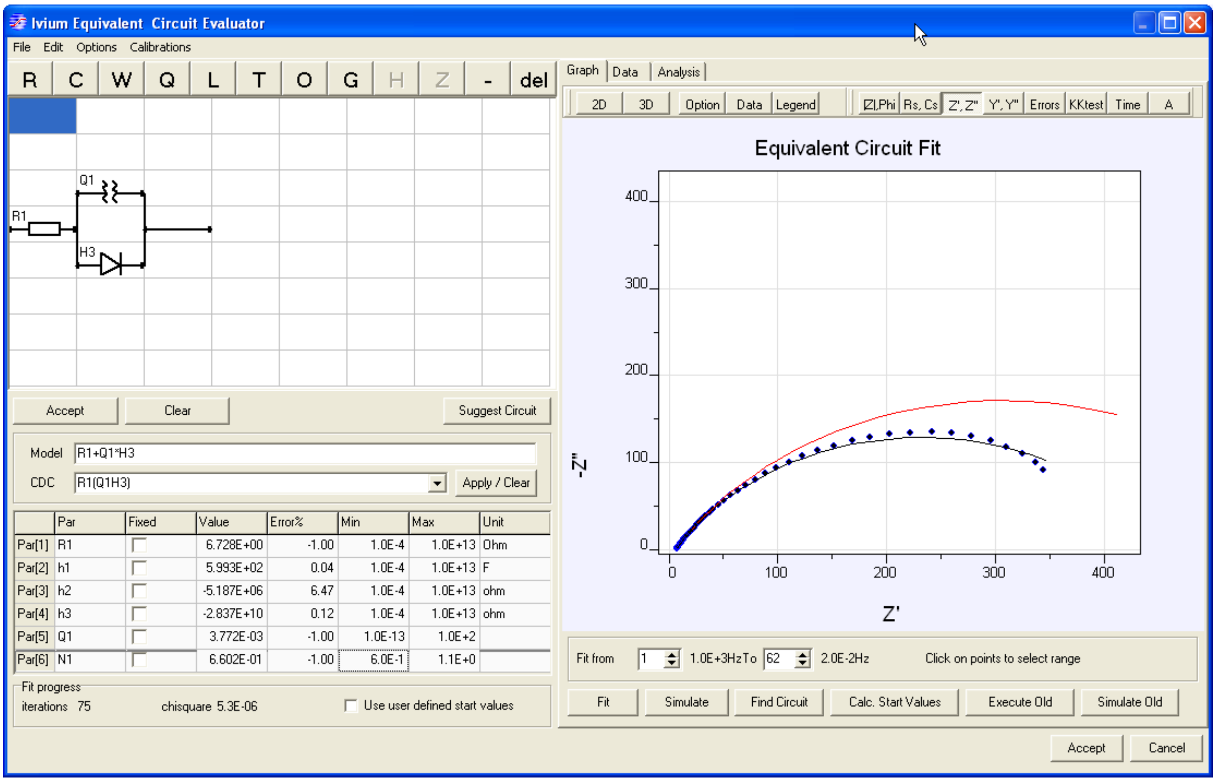
,that can be converted to differentials $h_n = (d^nE/dJ^n)$

$$h1 = 1/X1$$

$$h2 = -X2/X1^3$$

$$h3 = (2*X2-X1*X3)/X1^5$$

thus, the fitting results h1, h2, and h3 can be used to determine physical parameters. The fitted h1,h2,h3 from Figure 6 do define X1,X2,X3, from which directly follows J0, Ba,Bc.



Model R1+Q1*H3

CDC R1(Q1H3)

	Par	Fixed	Value	Error%	Min	Max	Unit
Par[1]	R1	☐	6.728E+00	-1.00	1.0E-4	1.0E+13	Ohm
Par[2]	h1	☐	5.993E+02	0.04	1.0E-4	1.0E+13	F
Par[3]	h2	☐	-5.187E+06	6.47	1.0E-4	1.0E+13	ohm
Par[4]	h3	☐	-2.837E+10	0.12	1.0E-4	1.0E+13	ohm
Par[5]	Q1	☐	3.772E-03	-1.00	1.0E-13	1.0E+2	
Par[6]	N1	☐	6.602E-01	-1.00	6.0E-1	1.1E+0	

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Fit from 1 1.0E+3HzTo 62 2.0E-2Hz Click on points to select range

Figure 6: Corrosion of Steel in 0.25M KCl, impedance scan 1kHz-20mHz, at OCP with 100mV amplitude, fitted to circuit with series resistor, parallel CPE and the nonlinear H

J : current density
J_0 : exchange current density
Ba : Tafel slope, anodic
Bc : Tafel slope, cathodic
E : potential, relative to the equilibrium potential

Appendix 2: Equations and definitions

The results can be expressed as Taylor expansions:

Potentiostatic:

$$I = (dI/dE)\,E + 1/2\,(d^2I/dE^2)\,E^2 + 1/6\,(d^3I/dE^3)\,E^3 + \ldots$$

$$= \quad Y_1\,E + 1/2 \quad Y_2\,E^2 + 1/6 \quad Y_3\,E^3$$

or galvanostatic:

$$E = (dE/dI)\,I + 1/2\,(d^2E/dI^2)\,I^2 + 1/6\,(d^3E/dI^3)\,I^3 + \ldots$$

$$= \quad Z_1\,I + 1/2 \quad Z_2\,I^2 + 1/6 \quad Z_3\,I^3$$

with $Z_1 = (dE/dI)$ $\quad Z_2 = (d^2E/dI^2)$ $\quad Z_3 = (d^3E/dI^3)$

with Z as impedance and Y as admittance (complex).

When we construct the experimental higher order impedances, we refer these to the perturbing signal. These relations are derived from the Taylor expansions.

Potentiostatic

$Y_1 = (I_1-3I_3)/E_1$ $\quad Z1 = 1/Y_1$

$Y_2 = 4I_2/E_1^2$ $\quad Z2 = -Y_2/Y_1^3$

$Y_3 = 24I_3/E_1^3$ $\quad Z3 = (3Y_2^2-Y_1Y_3)/Y_1^5$

Galvanostatic

$Z1 = (E_1-3E_3)/I_1$

$Z2 = 4E_2/I_1^2$

$Z3 = 24E_3/I_1^3$

Thus, the higher order Bode-, Nyquist- plots are constructed. Note that every order impedance is complex with imaginary and real parts, so each has a magnitude and phase angle. As the impedances are defined relative to the perturbing base frequency, the phase plots of the higher harmonics display the shift with respect to the base harmonic. The higher order observed phase shifts may therefore become larger than conventional ones, as the degrees/radians refer to their own harmonic period.

Appendix 3: Induced DC bias, "The Faraday rectification effect"

The even orders, induce a DC component alongside their higher harmonics, see Figure 1. This is sometimes called the "Faraday rectification effect"[9]. If there are no series components to the nonlinear component, the potentiostat will correct for this. However when there is a series component (resistor), a complication might arise.

Suppose we apply potentiostatic a voltage over a cell with a nonlinear component. The cell will respond with a range of current harmonics. The 2nd order (and 4th, 6th, etc.) will also create an extra

DC current on top of the “normal” DC current. The potentiostat will provide this extra current, while still maintaining the applied set DC potential. However, if there is a series resistor to the nonlinear component, that extra DC current will induce a voltage drop over this resistor, and the local DC voltage over the nonlinear component is no longer the “operator selected potentiostat-applied” DC bias.

The shift in DC bias voltage over the nonlinear component will move the equilibrium potential slightly, affecting the “quasi DC equilibrium state” of electrode kinetics and mass transfer. To account for this, theoretical models would need to be applied, and the universal applicability of the tool would be lost. However, this effect is usually small enough to neglect. To avoid making such errors inadvertently, the Ivifit tool will display a warning when the induced local voltage shift exceeds 2mV.