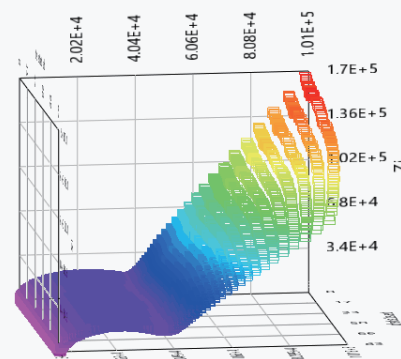


Yappari - a free software package for multiple datasets analysis in impedance spectroscopy

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Electrochemical impedance spectroscopy (EIS) is a well-established technique analyzing the response of a system to an oscillating excitation, usually a sinusoidal voltage. If the system satisfies conditions of causality, linearity and stability, its response to this excitation can provide information about its characteristics. Concerning EIS analysis there are some recent developments that need to be emphasized. One of them is the development of the calculation of distribution of relaxation times (DRT) and another is the ability to measure faster. These important advances, particularly the last, require the possibility to analyze multiple datasets. By multiple I understand thousands of datasets, sharing the same electrical model circuit. The program described here does both DRT analysis and nonlinear least squares optimization on multiple datasets.



Yappari stands for “Yet Another Program for Analysis and Research in Impedance”. Electrochemical impedance spectroscopy (EIS) is an ubiquitous experimental technique that analyzes the transfer function of a system (a sample, be it a solid, a composite, a liquid or an interface) to an oscillating excitation (AC). By transfer function we understand the relationship between the output signal of a linear and time independent system to the input signal. The time independent is a condition difficult to maintain in EIS, either because of external parameters (sample stability, temperature, humidity ...) or intrinsic ones, like charging a battery during the measurement. In EIS, the excitation is typically a small sinusoidal voltage and the measurement of the resulting current, both the amplitude and its phase, that passes through the sample. It is also possible to source an AC current and sense the voltage and its phase as it is also possible to measure samples with four-contact probes; these two methods are seldomly used.

The measurement is made at several frequencies, typically 10 points per frequency decade and in logarithmic scale, usually between 10^6 Hz to 10^{-3} Hz which correspond to time scales of regular physical-chemistry processes. A comprehensive description of EIS was just published^[1] and the interested reader can consult this paper and references therein for a fuller description than this brief note.

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Applications

This apparently simple method has many applications, it started around 1950 and it is used today in many fields^[2]. EIS can be used for classical electrochemistry research^[3] or for measuring properties of biological samples^[4], in dielectric spectroscopy^[5], for electrical characterization of materials^[6], for related techniques like electrochemical impedance tomography^[7] and others. Basically, physical-chemical processes like diffusion, electronic transport, interfaces can be modeled by simple electric circuits or by their combinations : resistance, capacitance or more complex models. These circuits have well defined transfer functions. If we know the transfer function, the response of an electric circuit to an AC signal at a given frequency can be calculated and this simplicity is the advantage of using EIS. Each circuit element should be associated with physico-chemical processes and generally have a specific relaxation time. For instance, ionic diffusion is typically a slow process hence with slow relaxation time.

One limitation is that one needs to make suppositions of the physical model (or electrical circuit) to use for a given sample. So one needs to make an *a priori* hypothesis that the system tested will behave following a physical model. This is an important limitation of EIS and a source of controversy in analyzing the same system with different models. For some systems, like fuel cells or batteries, modeling an equivalent electrical circuit can be rather difficult.^[8]

In recent years some great advancements have been made towards predicting the number of processes involved and their relaxation times, particularly for fuel cell analysis or bat-

teries^[8–16], to cite just a few. These methods are typically referred to as “Distribution of Relaxation Times” (DRT) and the interested reader can consult these references.

A DRT method does not require an *a priori* knowledge of the physical process, on the contrary, it can provide a basis for building a model. This is an advantage, even though this technique has its own limitations since it involves fitting ill-determined systems, sometimes in the presence of noisy data^[17]. Moreover some circuit elements cannot be analyzed with this technique or may require data processing.^[18]

A second development that merits attention is the ability to acquire data faster. This is rather difficult to achieve by classical sweeping frequency method, as the time of the measurement depends on the measurement frequency. A typically standard EIS measurement for the usual 8 or 9 decades of frequencies can take hours or even more if low frequencies are measured. However, several methods have been developed to accelerate data acquisition. The simplest idea is to use multiple frequency excitations and acquire data at these frequencies simultaneously; this has been implemented in some commercial instruments. Other methods involve the use of non-sinusoidal signal excitations and can provide very fast measurements^[18,19,20]. These non-sinusoidal excitation methods can be very fast but their application brings about other questions about stability or equivalency to the classical EIS.

Nevertheless, even with classical acquisition systems, by adjusting the frequency domain to the timescales of processes of interest, several thousand datasets can be acquired in a matter of days or more (as an example, in my laboratory we have measured the dielectric properties of a samples during 30 to 45 days continuously.^[21] Therefore, there is a need to develop computer programs and methods that include both DRT calculations and circuit modeling of multiple datasets. Most of the available packages are used for fitting a single dataset either by DRT or non-linear optimizations. Python scripting with available packages is another possibility but requires quite advanced software knowledge.

The question one may ask, in relation to the title of this paper, is what “multiple” means? One dataset means an array of frequencies, typically about 100 values, and a complex impedance signal for each frequency point. In terms of memory of a computer this is far from challenge but calculations will involve inverting matrices and this will be the determining factor in the number of datasets that can be analyzed. The program described here can process thousands of datasets in a batch. For a regular desktop PC of 2023, fitting 1000 datasets will take roughly a few minutes depending on the circuit complexity and starting point.

Methods

DRT calculations can be made starting from the observation that for a given number of parallel RQ units (Q is a Constant Phase Element) connected in series with a resistor R_0 , the total impedance can be expressed as the sum of each contribution for all frequencies.^[9,12,14]

$$Z(\omega) - R_{HF} = R_{pol} \int_{-\infty}^{+\infty} \frac{G(\tau) d\ln(\tau)}{1 + i\omega\tau}$$

where R_{pol} , or polarization resistance is equal to $R_{tot} - R_{HF}$; R_{tot} is

the total resistance of the circuit and R_{HF} is the resistance at the highest frequency. The integral in the previous equation can be written as:

$$\mathbf{AG} = \vec{b}, \vec{b} \equiv \vec{Z}_{re} - R_{HF}$$

with the elements of matrix as, for the real part:

$$A_{m,n} = \frac{R_{pol} \delta \ln(\tau_n)}{1 + \omega_m^2 \tau_n^2}, \delta \ln(\tau_n) = \ln(\tau_{n+1}) - \ln(\tau_n), \tau_n = 1/\omega_n$$

And for imaginary part:

$$A_{m,n} = -R_{pol} \frac{\omega_m \tau_n \delta \ln(\tau_n)}{1 + \omega_m^2 \tau_n^2}, \delta \ln(\tau_n) = \ln(\tau_{n+1}) - \ln(\tau_n)$$

with the condition:

$$\int_{-\infty}^{\infty} G(\tau) d\tau = 1$$

This is an ill-conditioned system and one needs to use, for instance, a regularization approach with an estimate of the solution as:

$$b = (A^T A + \lambda^2 I)^{-1} A^T Z$$

where I is the identity matrix and λ is the Tikhonov regularization parameter^[22].

This system can be solved in this program for either real or imaginary part of impedance, or for both. Data should be acquired with log spacing, the program has the option to interpolate the data to a given number of datapoints scaled in log space.

There are three methods used now in Yappari for DRT calculations: a regularization parameter method developed by C. Altenbach for EPR spectroscopy^[23], a derived method proposed by Fisk^[24] and a Gold optimization method.^[25,26] Criteria for selecting the optimal regularization parameters are included in this program, they are based on the mean square error between the experimental Z_r and Z_i and the recalculated impedances from the DRT. More powerful DRT packages are available, see for instance the programs of Ciucci et al. albeit, to the best of my reckoning, limited to a single dataset.^[16,17,27,28]

For the non-linear fitting we use one of three popular algorithm methods available: Trusted Region Dog Led algorithm (TRDL), Constrained Levenberg Marquardt (CLM), and Levenberg Marquardt (LM). For TRDL and CLM, the fit is constrained to intervals defined by the user. The program allows an easy building of an electrical model from about thirty defined circuits and that can be selected in a GUI interface.

Other functions

Spectra can be simulated for user designed circuits. Experimental data can be read from various files including user defined ASCII files. The program has several graphic panel windows : Nyquist and Cole plots together with a 3D plot of selected datasets, either in Nyquist, Z_r or Z_i or their difference, as selected by the user.

In EIS there should be a correlation between the real part and the imaginary part of the measured impedance. This can be checked upon by the Kramers-Kronig method or by Hilbert transform. The latter, named Z-Hit and implemented in this program, is a transform of the phase into the absolute

part of the impedance, for one or many datasets.^[29]

Impact

This package can be useful for dealing with many datasets, for instance obtained during a slow evolution of the temperature. It has the advantage of combining two different techniques (DRT and non-linear least squares) in a single package. The program has been used in my laboratory recently, for instance in this publication^[30]. It has also been described in a blog post of a producer of impedance measurement instruments.^[31]

Limitations

The current version of the program can generate a limited number of circuits (several hundredths, nevertheless) so this part might be improved in future upgrades.

■ CONFLICT OF INTEREST

The authors declare no conflict of interest.

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