NFRA

(An Introduction)

ZAHNER

06/2022

Table of content

1 NFRA – an extension to EIS

Electrochemical impedance spectroscopy (EIS) is an established characterization technique for the analysis of different electrochemical systems. Like cyclic voltammetry (CV), EIS is an "active" method where one induces a change ("excitation") in a characteristic system variable, e.g., the voltage, and monitors the change ("response") of another system variable, e.g. the current. To get reliable EIS results free of artefacts and within sufficient accuracy, some conditions must be fulfilled. These conditions are stationarity, stability, causality, and linearity of the system under investigation (SUI). Stationarity implies that the SUI must be at steady-state, during EIS measurement. Causality implies that a cause must lead to an effect – any change of the response magnitude must be caused by a change in the excitation magnitude. Last but not least, to benefit from the elegant modelling rules derived for EIS, we need linearity. This means that the SUI must behave approximately linear within the deflection limits of the excitation.

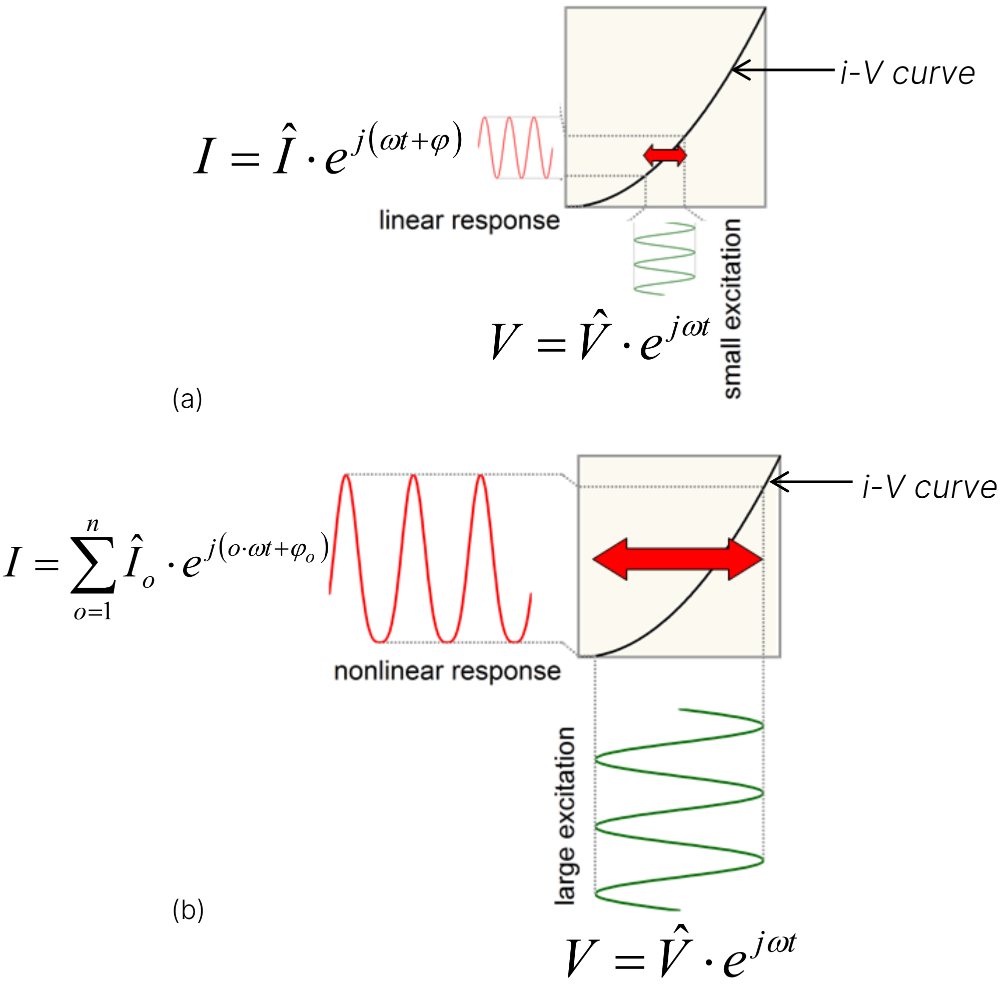


Fig. 1: (a) EIS and (b) NFRA excitation signals and the corresponding responses.

In Fig. 1(a), due to the prerequisite of linearity, only a small excitation signal can be applied for EIS. With this small excitation signal, only the linear aspects of the processes in a small voltage interval are observable and to analyse the whole i-V curve, multiple EIS measurements (with small excitation signal) at different bias potentials must be carried out. Afterwards, results from the measured EIS spectra are assembled and a complete overview of the system is obtained. This is a time taking process which requires multiple EIS measurements and post-processing of the measured data. For numerous applications, a measurement process is desirable which can unveil the linear and nonlinear characteristics of a system in a fast single measurement. These requirements can be fulfilled with the nonlinear frequency response analysis (NFRA).

Fig. 1(b) shows the excitation and response signal for an NFRA. Compared to EIS, the amplitude of the excitation signal is large. This large excitation signal over a non-linear i-V curve part leads to the simultaneous characterization of both linear and nonlinear properties and the response signal is obtained in the shape of a distorted signal. This nonlinear response signal is then further processed to get the desired results (explained later).

2 EIS vs NFRA: excitation and response signals

For EIS or NFRA, a voltage (or current) excitation signal is applied to the SUI in the form of a sine wave with an angular frequency (ω). In the following, voltage signal is used as an excitation signal.

$$V = \hat{V}.e^{j\omega t} \tag{1}$$

Here, $\hat{V}$ is the amplitude of the excitation sine wave and t is time. The response to voltage excitation (Eq. 1) can be described with the following equation.

$$I = \sum_{o=1}^{n} \hat{I}_o \cdot e^{j(o\cdot\omega t+\varphi_o)} \tag{2}$$

$$I = \hat{I}_F \cdot e^{j(\omega t+\varphi_F)} \quad + \quad \sum_{o=2}^{n} \hat{I}_o \cdot e^{j(o\cdot\omega t+\varphi_o)} \tag{3}$$

In return to the single frequency based excitation signal, Eq. (2) shows the response signal which incorporates multiple sine waves with different frequencies. Here, $\hat{I}_o$ is the amplitude of the response sine waves and φ_o is the phase shift between the response and excitation signals. The subscript “o” defines the order of the sine waves in the response signal. The first order (o=1) defines the response with the fundamental frequency (frequency of excitation signal). The magnitude of this first-order response (fundamental response) is $\hat{I}_F$. The part of the response signal with frequencies as multiples of the fundamental frequency (o=2,3,4.....n) are defined as harmonics. In Eq. (3), the response signal is divided into its two corresponding fundamental and harmonics parts. The harmonics in the response signal are observed due to the non-linear behaviour of the system under investigation provided that the excitation signal consists of a single frequency.

The fundamental response is used to calculate the impedance. The harmonics provide us with additional information about the system and are used to further characterize the system under investigation. This additional information is not obtainable in EIS.

In EIS, since a small excitation signal is used hence the nonlinear part of the response signal is close to zero and the response signal consists majorly of linear part with the fundamental frequency (see Fig. 1). In EIS, the harmonic share in excitation and response signal is used to determine the accuracy of the EIS via weighted harmonics autocorrelation.

In EIS

- the shape and wavelength of the excitation and response signal stay the same
- amplitude and the phase changes

In NFRA, the response signal is distorted and its shape is not the same as that of the excitation signal (see Fig. 2).

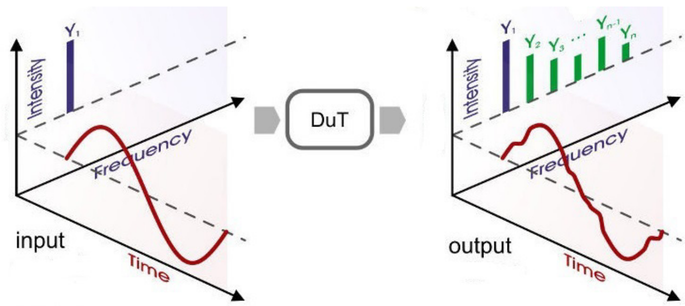


Fig. 2: Excitation and response signals in nonlinear frequency response analysis.

The distorted response signal can be reproduced with the addition of multiple sine waves of different frequencies (fundamental frequency and its multiples). To illustrate this phenomenon, a distorted signal in Fig. 3 is constructed with the addition of fundamental frequency (*f*) and three additional sine waves with different frequencies (odd multiples of the fundamental frequency).

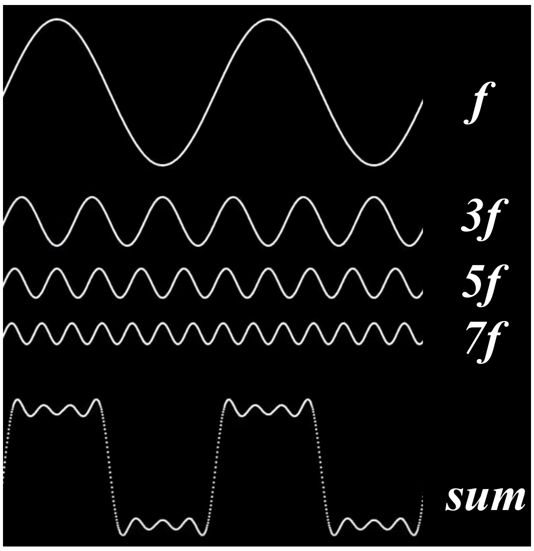


Fig. 3: Addition of multiple sine waves to produce a distorted signal (here a square wave).

For a distorted signal, the frequency, the phase shift and the amplitude of the individual sine waves needed to reconstruct the distorted signal can be determined with the Fourier transformation (FT). With the FT, a signal in the time domain can be converted into the corresponding signal in the frequency domain. In computer-based data acquisition systems, the FT is realized usually in the form of the discrete fast Fourier transform (DFT). Similarly, in NFRA, the distorted response signal in the time domain is converted into the response signal in the frequency domain via DFT (see Fig. 2).

In Fig. 2, a sine wave (single frequency) with large amplitude is used as an excitation signal. This leads to a distorted response signal which is subsequently reconstructed with sine waves of multiple frequencies. The Fourier response is described with Y_1, Y_2, Y_3 and so on in Fig. 2. This response signal is expressed with Eq. 3, in which the response signal has an impedance part at the fundamental frequency and an additional part containing harmonics, contrary to EIS.

$$I = \hat{I}_F \cdot e^{j(\omega t + \varphi_F)} + \sum_{o=2}^{n} \hat{I}_o \cdot e^{j(o \cdot \omega t + \varphi_o)}$$

quotation with $V = \hat{V} \cdot e^{j\omega t}$ ↓ Linear part (for calculating the impedance[1])

Harmonics ↓ Nonlinear part (provides additional insight)

3 NFRA prerequisites

Up to this point, it is clear that in EIS, the response signal is only comprised of a linear part (with fundamental frequency), whereas in NFRA, the total response is comprised of two parts, fundamental and harmonics. In NFRA, harmonics should only be caused by the large excitation signal. No other phenomenon should contribute to the harmonics. If that is not the case then NFRA results will be contaminated by artefacts and cannot be used to reliably analyse the SUI. It is known in EIS, that the following phenomena cause harmonics in the response signal:

- Instability of the system under investigation
  - Non-steady state conditions - time drift
  - Electrochemical or mechanical noise (pitting corrosion, gas bubbles, stirring)
- External electrical interferences (line frequency, ground loop, ESR/NMR devices nearby)
- Instruments limitation (in particular potentiostat flaw at higher excitation frequencies)
- High amplitude excitation signals (intended in NFRA)

[1] *Impedance calculated from the linear part of NFRA is not the same as the impedance from EIS. The impedance value will tend to the traditional EIS impedance value with a smaller harmonic share*

Hence in NFRA, it must be made sure that the harmonics are only caused by the high amplitude excitation signal and not by other phenomena. The researcher should facilitate this by avoiding electrical or mechanical interference, by providing an optimal design of the experimental setup regarding shielding and wiring and by ensuring the artefacts-fee steady-state operation conditions. It is desirable that the disturbing influence of residual, unavoidable or intended time drift (what may happen e.g. during charging or discharging of batteries) may be cancelled too. Zahner's potentiostats can do this via automatic "online drift compensation" during measurement (*in-situ*). In addition, it is also crucial that the signal generator in the potentiostat produces accurate sine wave excitations (see "Harmonics in excitation signal" below) with well-controlled amplitude. A distorted sine wave excitation will introduce (unavoidable) harmonic content even in the case of linear system response and this will lead to faulty measurements. Also, if the amplitude of the excitation produced by the signal generator is not the same as intended then this will lead to errors in the NFRA results because the harmonic response greatly depends on the amplitude of excitation signals. To carry out accurate and reproducible NFRA measurements follow the process given below:

1. Measure EIS
   i. Make sure that harmonic distortions are minimized
2. Measure NFRA

NFRA is only possible if the potentiostat can generate accurate sine waves and properly measure the distorted response signal and the software can convert (in-situ) the distorted response signal from the time domain into the frequency domain.

Harmonics in excitation signal:

Producing a perfect sine wave excitation signal is not possible. The semi-perfect excitation signal results in the minute harmonic share in the FFT of the excitation signal (Eq. 4).

$$V = \hat{V} \cdot e^{j\omega t} + \sum_{o=2}^{n} \hat{V}_o \cdot e^{j(o \cdot \omega t)} \tag{4}$$

In Eq. 4 the summation term represents the harmonic share in the excitation signal. Such a distorted excitation signal will lead to additional harmonic share in the NFRA (Eq. 5).

$$I = \hat{I}_F \cdot e^{j(\omega t + \varphi_F)} + \sum_{o=2}^{n} \hat{I}_o \cdot e^{j(o \cdot \omega t + \varphi_o)} + \sum_{o=2}^{n} \hat{V}_o \cdot e^{j \cdot o \cdot \omega t} / Z_o \tag{5}$$

Zahner (in-situ) measures the harmonic share from the excitation signal and then directly use it in the response to mitigate its effect on the harmonics in the response signal. In Eq. 5, the Z_o is the "impedance at the frequency of the harmonic".

Fig. 4 shows the example of harmonics in the excitation signal. For accurate NFRA measurements, the effect of these harmonics should be eliminated from the harmonics response of the NFRA.

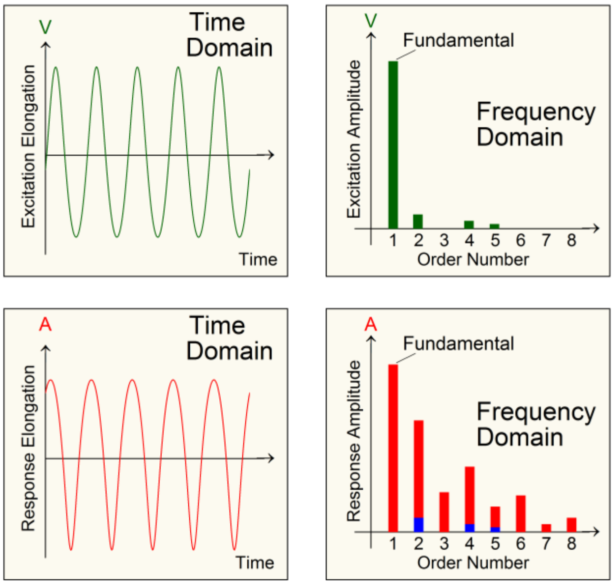


Fig. 4: Harmonics in excitation signal and their corresponding effect in the response signal.

4 Pro and contra of NFRA

Pro: EIS is an established technique to characterize electrochemical systems. However, EIS is not able to directly observe the non-linear aspects of the processes under investigation (explained before, see Fig. 1), whereas the NFRA can, besides impedance, directly provides additional insights into the non-linear electrochemical processes in a single run.

Contra: EIS results can be explained usually by means of linear combinations of well-established analytical formulas. These combinations can be represented by equivalent electrical circuit (EEC) models built from for instance resistors, capacitors plus specific impedance elements directly assigned to the processes happening. In contrast, NFRA solutions are normally calculated using numerical approximations due to the usually much higher complexity of the basic transfer function. Since compared to EIS, not much work has been done in the field of NFRA, a well-known model based on analytical solutions is usually not available from the literature. Therefore numerical models have to be usually developed for every special case separately.

5 NFRA modelling

NFRA results are usually obtained via numerical approximation. For NFRA modelling, the process given below is usually followed.

1. Write an algorithm to calculate the current-voltage relation in the time domain for the system under investigation, considering
    a. Time- and site-dependent concentrations
    b. Mass flows
2. Start numerical simulation from a steady-state.
3. Simulate an infinitesimal change vs time, eventually developing the change into sinusoidal excitation vs time (equivalent to a certain frequency).
4. After some sine periods, calculate the harmonics from response via fast Fourier transformation.
5. Repeat steps 2-4 for all the interested frequencies.

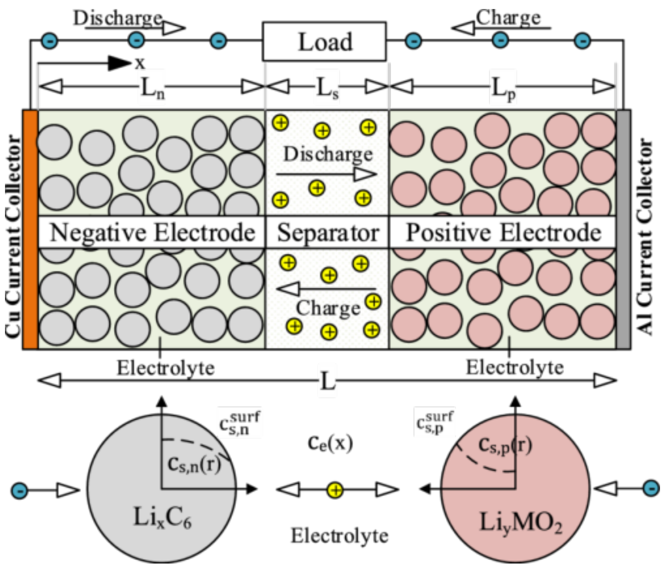
Example
System for modelling

To better understand the NFRA modelling process, an example is taken from research conducted in "Institute of Energy and Process Systems Engineering". In which they modelled a 2-dimensional Li-ion battery for NFRA with the following simplifications

- The active materials in the battery are spherical.
- All active materials are identical (geometrically, physically and chemically)

In 1-D modelling, a simplification in addition to what is described before in the 2D model is also considered

- No significant gradient is present in the electrolyte phase (only valid for very low current density)



Logarithmic model

For the above explained simplified battery model, an **analytical solution** for the current-voltage relation in the time domain is built on the basis of

1.	1st and 2nd Ficks' law	(for solid-phase Li concentration in Li_xC_6)
2.	Faradays' Law	(for Li^+ flow at the particle surface)
3.	Butler-Volmer	(charge transfer at the solid-separator-interface)
4.	Faradic efficiency	
5.	Double layer capacity	

Afterwards, finite element modelling (FEM) is used to create a mesh where each discretized element contains the analytical solution (prepared in the logarithmic model). The mass and charge transfer for a current excitation are modelled in the mesh between multiple discretized elements via **numerical approximation**. From this model, a voltage response is calculated for the provided current excitation. Eventually, the excitation signal is increased from a small excitation to a frequency and the voltage response is calculated via finite element modelling. Next, the voltage response is converted from the time domain to the frequency domain via FFT. This provides the NFRA results (fundamental and harmonics) for an excitation frequency (see Fig. 6).

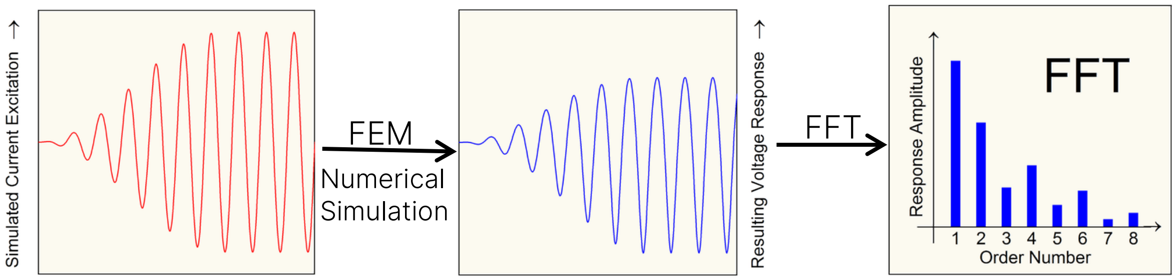
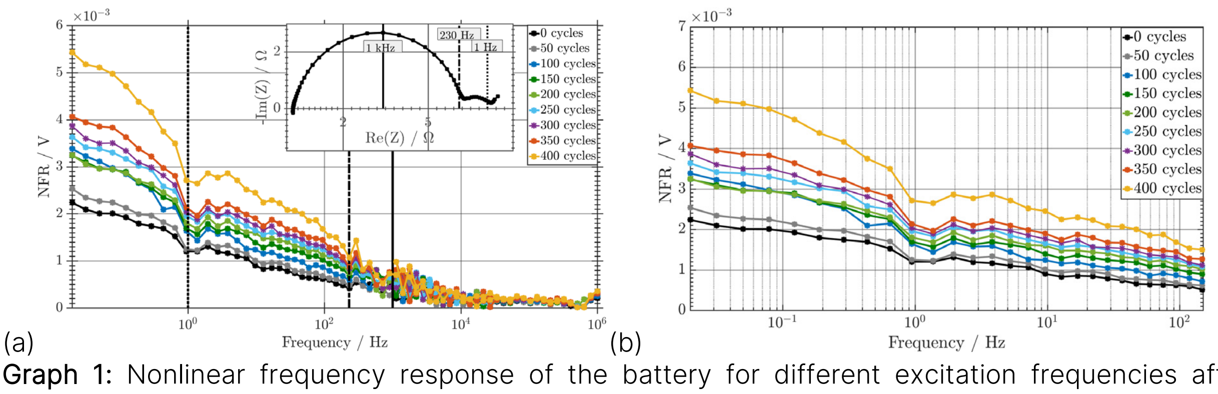


Fig. 6: Voltage response calculated via numerical approximation for a current excitation in a simplified Li-ion battery model

This process is then repeated for all the excitation frequencies. From FFT results, impedance is calculated from the linear response signal (response signal with fundamental frequency). This response signal is used to plot the Nyquist or Bode plot. Harmonics can also be plotted against excitation frequency to see the corresponding change. These harmonics are especially sensitive to symmetrical states or processes (explained later).

For the simplified Li-ion battery model, the final NFRA modelling results are shown in the graph below[2].



Graph 1: Nonlinear frequency response of the battery for different excitation frequencies after multiple aging cycles

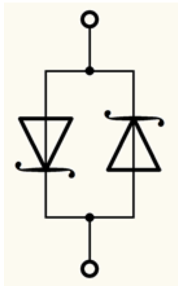
It is clearly visible that at the high frequencies the change in NFR is not much. However, at low frequencies change is sufficiently big to show the aging process. Using this database, a few NFRA measurements at low frequencies can provide us

[2] *This example is taken from the peer-reviews Journal of Applied Sciences Harting et. al., Appl. Sci. 2018, 8, 821; DOI: 10.3390/app8050821*

with enough information so that an estimation of battery age can be made. This process is very fast and includes the linear and nonlinear processes of the battery.

NFRA works at low frequencies (up to some 100 Hz).

Butler-Volmer system (an analogy)



Butler-Volmer behaviour can be simulated with two anti-parallel Schottky-diode elements connected as shown on right. The electrical behaviour of these Schottky diodes depends greatly upon the temperature, so an i-V curve is measured at 298 K. Afterwards, the NFRA measurements are carried out on the Schottky diodes. An i-V curve, Nyquist plots and the corresponding harmonics for 3 different excitation signals are shown in Fig. 7. The i-V curve is measured for a charge transfer coefficient (α) of 0.5 and a bias current of 10 * J_o (exchange current) and the excitation alternating current signal has an amplitude of 10 * J_o.

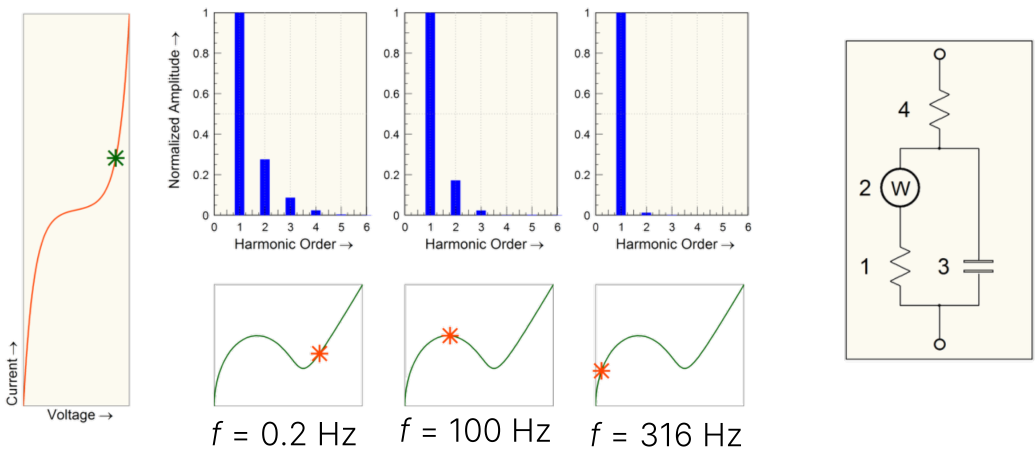


Fig. 7: i-V curve and NFRA measurement on anti-parallel Schottky diodes. The EEC for the fitting of the Nyquist plot is shown on right.

From Fig. 7, it is visible that harmonics are nearly diminished at a frequency of 316 Hz that's why it is not useful to do NFRA at frequencies above 100 Hz. At high frequencies, the capacitor in the EEC behaves as a short circuit and then the combined non-linear behaviour of the resistor and Warburg is bypassed.

When the bias current (of 10 * J_o) is removed then the harmonics at the even multiples of the fundamental frequency vanishes (see Fig. 8). This indicates that the harmonics are really sensitive to the symmetry (potential/current bias symmetry).

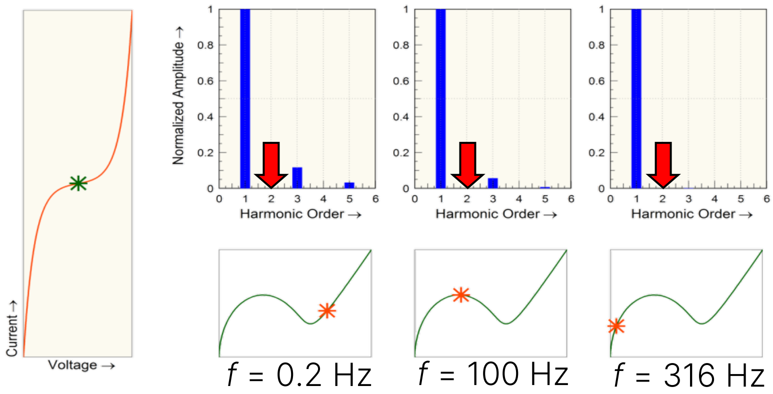


Fig. 8: Harmonics in NFRA measurement for Schottky diodes at the excitation signal of 10 * J_o and α = 0.5.

Now when α is changed from 0.5 (symmetry) to 0.4 (asymmetry) then the harmonics are modified (see Fig. 9). The harmonics are very sensitive to any asymmetry (current bias or current charge transfer coefficient (α)). This information is not available in EIS directly but can be seen in-situ in NFRA.

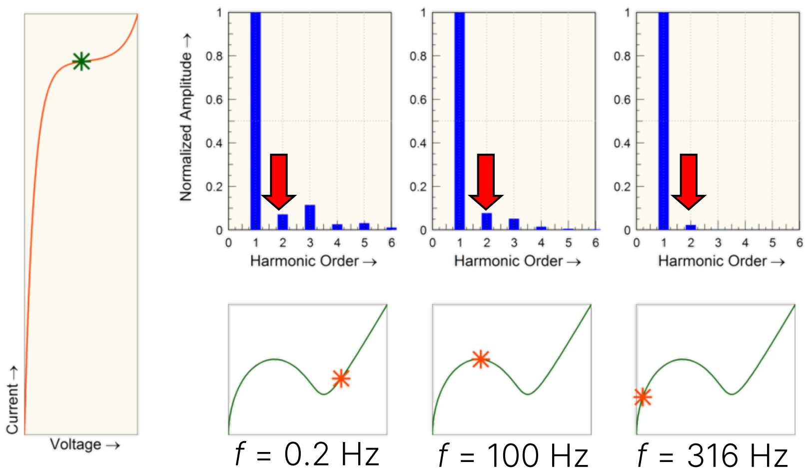


Fig. 9: Harmonics in NFRA measurement for Schottky diodes at the excitation signal of 10 * J_o and α = 0.4.

Technical requirements

The first technical requirement of a potentiostat for use in NFRA measurement is accurate sine wave generation. If the sine wave is not of the same amplitude as intended then the harmonics will contain an error, because the harmonics depend greatly upon the amplitude of the excitation signal. In addition, the signal generator should generate a perfect sine wave; otherwise, the harmonics will contain the false response signals which will lead to the false analysis of the system.

The potentiostat should be able to produce and process the sine wave and the software must be able to convert the sine waves from the time domain to the frequency domain during the process.

The potentiostat should treat both the excitation signal and response signal similarly as shown in Fig. 10. This will ensure that the gain and phase shift (G* coefficient)[3] will be the same for the excitation and response signal. Zahner's potentiostats deal with both signals in the same way hence both coefficients in excitation are response signal are same and got cancelled in EIS.

$$I = G_I^* \cdot \hat{I} \cdot e^{j\omega t} \quad \& \quad V = G_V^* \cdot \hat{V}_F \cdot e^{j(\omega t + \varphi_F)} , \qquad G_I^* = G_V^*$$

Whereas in NFRA, the coefficient for harmonics has to be measured for the potentiostat and therefore a calibration is required to acquire the correct results.

$$V = G_{V_F}^* \cdot \hat{V}_F \cdot e^{j(\omega t + \varphi_F)} + \sum_{o=2}^{n} G_{V_o}^* \cdot \hat{V}_o \cdot e^{j(o \cdot \omega t + \varphi_o)}$$

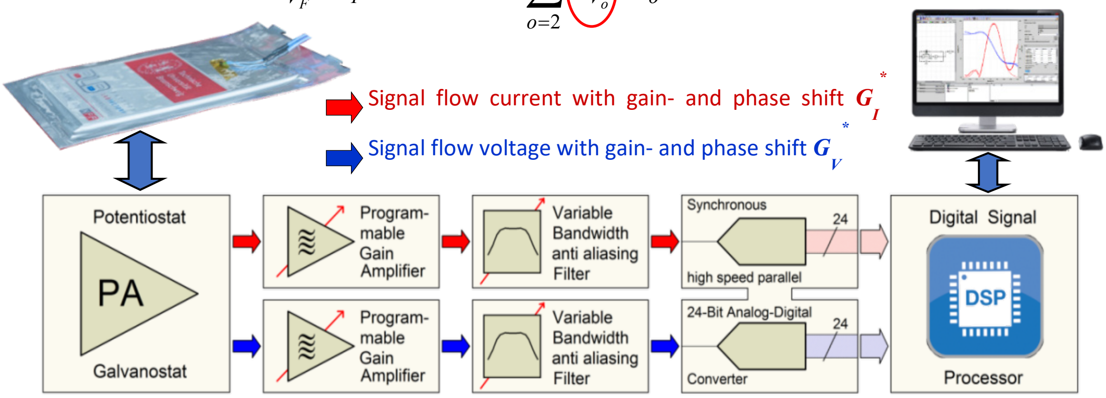


Fig. 10: Identical signal processing signal process for the excitation and response signal during EIS and NFRA.

A calibration table is required to correctly process the gain- and phase shift coefficient at harmonics.

Calibration

To perform the calibration process, two anti-parallel Schottky diodes are used. These antiparallel Schottky diodes exhibit a current-voltage curve similar to the Butler-Volmer curve.

For calibration, the following process is carried out

1. Acquire an i-V curve from the diodes with the voltage interval equivalent to sine wave amplitude (see Fig. 10a).
2. For a theoretical sine wave (blue in Fig. 11), map a distorted voltage sine wave (see Fig. 11b).
3. Convert the distorted sine wave from the time domain to the frequency domain via FFT.
4. Perform a NFRA experiment with all frequencies of interest (see Fig 12).

[3] * indicates complex magnitude

5. Divide the FFT results from step 4 with FFT results from step 3 to get the calibration table.

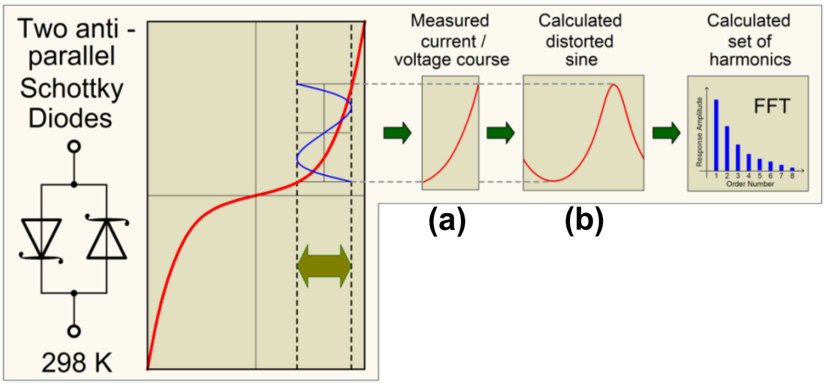


Fig. 11: Calculation of the distorted signal, with mapping a sine wave for a specific voltage interval.

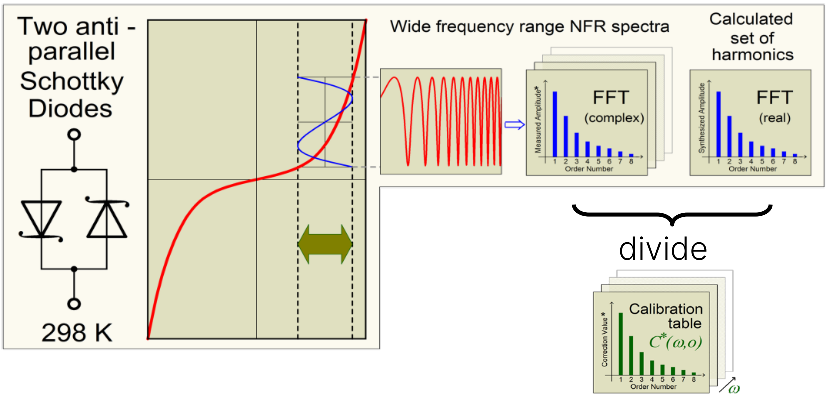


Fig. 12: Calibration table for different frequencies for accurate NFRA measurements.

In Summary, NFRA is an extension of EIS which allows the measurement of linear and non-linear processes in a single run. It must be made sure that the harmonics are only because of the large amplitude and not because of the artefacts. NFRA results are only perfectly fitted with numerical modelling. This means that for every system a new model has to be built which will work only for that specific system and will not work for some other system. The potentiostat should be able to generate accurate sine waves and should be able to process the sine wave. The software should be able to convert (in-situ) the sine wave from the time domain to the frequency domain via FFT. For each system, a calibration table is also required to accurately measure the harmonics.

NFRA not only incorporates the linear and nonlinear process in a single measurement but also provide more information than EIS which gives more insight into the system. NFRA is a potential technique for the different systems where a fast and accurate analysis of the system is required.