Development of Electrochemical Impedance Spectroscopy Instrument for Survey on Fuel Cell

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***Abstract*—After a description of Electrochemical Impedance Spectroscopy methods, a new instrument extremely cheaper than market ones and suitable for fuel cells investigation will be presented. The characteristics for the system will be calculated and presented also together with some measurements realized.**

Keywords – Instrumentation, Electrochemical Impedance Spectroscopy, Automatic test bench.

I. Introduction

Electrochemical Impedance Spectroscopy (EIS) studies the system response to the application of a periodic small amplitude alternating current (ac) signal. These measurements are carried out at different ac frequencies and, thus, the name impedance spectroscopy was later adopted. Analysis of the system response contains information about the interface, its structure and reactions taking place there [1]. It is a well known survey technique[1-5] and used in many applications like, e.g., determination of double-layer capacitance, ac polarography biomolecular interaction and microstructural characterization. Another very important application field is the characterization of fuel cell. In this field EIS represents a powerful diagnostic tool to characterize limitations and to improve the performance of fuel cells[6-8].

In this work, after a brief description of EIS technique for fuel cell analysis, it will be presented a new instrument to realize this technique. The instrument will be described both in the hardware part and in software one. Some experiment on fuel cells, able to validate the instrument functionality, will be also presented.

In literature others colleagues faced the problem as Bucci *et al.* [9] and Wingelaar *et al.*[10]which realized automatic test bench for fuel cells characterizations focusing their work on V/I and interrupt analysis, but they don't consider ac signals as input, or Ordonez *et al.* [11] which if realize a precise EIS system developed based on a Digital Signal Processor while in our work it has been personalized the laboratory instrumentations.

II. Description of EIS Technique for Fuel Cells Analysis

EIS is an experimental technique that can be used to characterize fuel cells. The idea is to send an ac signal over a range of frequencies inside the fuel cell; the ratio between the output signal and the input is its transfer function, including the energy storage and dissipation properties, which can modeled as a network of impedances and so represented and studied. In fact a passive complex electrical system comprises both energy dissipater (resistor) and energy storage (capacitor) elements. This model can well justify the three sources of voltage low typical of fuel cells: the kinetic losses corresponding to charge transfer activation, ohmic losses corresponding to ion and electron transport and concentration or "mass transfer" losses. Bode and Nyquist graph are often used to plot data obtained by EIS.

Figure 1 [7] well describes as is realized an EIS. The ac stimulus is provided by a frequency response analyzer (FRA) and is sent to the device under test (DUT) through a specific load. The ac voltage and current response is then analyzed by the FRA which determines the impedance - resistive, capacitive and inductive - behavior of the cell at that particular frequency. All the physicochemical processes occurring within the cell (electron & ion transport, gas & solid phase reactant transport, heterogeneous reactions, etc.) have different time-constants characteristic and therefore appear at different ac frequencies. Using a wide range of frequencies, impedance spectroscopy helps to identify and quantify the impedance associated with these different processes.

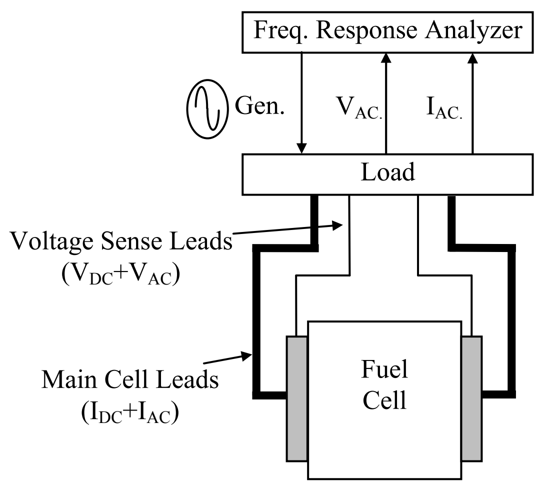


Figure 1. Instrument for EIS of fuel cells.

Depending by the kind of stimulus it is possible to have galvanostatic measurements or potentiostatic ones. Galvanostatic EIS involves the application of an ac current $I = I_m e^{j\omega t}$ (where Im is the maximum value of the current) and measurement, in steady state, the correspondent voltage response equal to $V = V_m e^{j\omega t'}$. Potentiostatic EIS measures the impedance by applying a sinusoidal voltage to the sample and measuring the correspondent current. Fixed this quantity the impedance of the device under test is given by:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = Z_m e^{j\varphi} = Z' + jZ'' \qquad (1)$$

where φ is the difference between the input and the output wave. Being Z(ω) the impedance and the transfer function of the system, its study provides a detailed description of the system.

The advantages of EIS are:

- Measurements can be made under real-world fuel cell operating conditions, e.g., open circuit voltage or under load (DC voltage or current).
- Multiple parameters can be determined from a single experiment.
- Relatively simple electrical measurement that can be automated.
- Can verify reaction models, and characterize bulk and interfacial properties of the system, e.g., membrane resistance and electrocatalysts.
- Within fuel cell functioning limit, measurement is non-intrusive – does not substantially remove or disturb the system from its operating condition.
- A high precision measurement – the data signal can be averaged over time to improve the signal-to-noise ratio.

A. Impedance Measurements Techniques

1) The electrochemical cell: Batteries (≈ 10^2 mΩ) and fuel cells (≈ mΩ) have a very low intrinsic impedance. This obliges to take particularly in account the connecting cables impedances during a measurements, which could have the same order of magnitude. Because the no ability from instrumentation to distinguish the impedance contribute due to cables and those joined to the DUT, a big uncertainty could accompany 2-terminals or 3-terminals measurements. 4-terminals techniques is the best technique because warranties the separation between the electrodes voltage drop and the cables one assuring high accuracy measurements[12].

The most simple cell study configuration uses two electrodes dip in a electrolyte. A voltage applied to the electrodes causes a current flow in the DUT. The electrodeas are commonly called Working Electrode (WE where is studied the interface between electrolyte and electrode) and Counter Electrode or Secondary Electrode (CE) which allows the current flux inside the DUT. This configuration is used to study the electrolyte properties. CE has a big surface, soon made of platinum, to have a very low impedance. When the WE reaction has to be controlled to manage voltage and current the presence of a third electrode is reached. Reference Electrode (RE) has a constant voltage and usually is in a section different than the WE is located. The two sections are connected by a thin glass tube that has the electrolyte inside. This configuration allows the separation between the volumetric properties from the interface ones. A 4-terminals configuration provides an analysis of the processes which appear inside the electrolyte between two electrodes separated by, e.g., a membrane. In this case the aim of the WE and CE is only to allow the flux of the current allowing the study of the ionic transportation through the membrane.

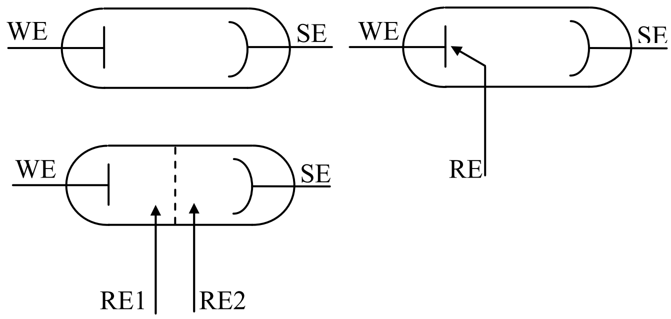
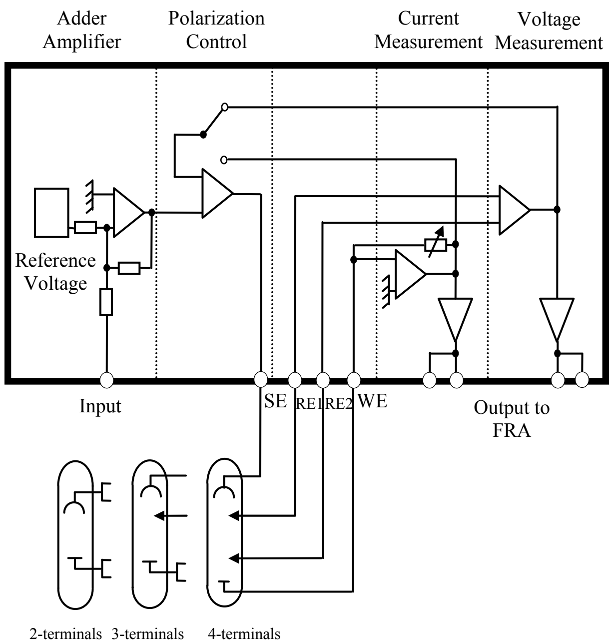


Figure 2. 2-terminals, 3-terminals, 4-terminals impedance measurement



techniques.

Figure 3. Electrochemical interface.

2) Electrochemical Interface (ECI): to allow the analyzed measurements Frequency Response Analyzer (FRA) able to provides the sinusoidal stimulus and pick up the output is necessary. This device often needs an electrochemical interface (Figure 3) to be adapted to the load.

It is composed by:

- Adder: provides the polarization voltage (potentiostat) or polarization current (galvanostat) for the cell summing an ac and a dc signal;
- A polarization control: avoids stability problems;
- Electrodes connections: the reference electrodes (RE1 and RE2) are used to measure the cell characteristics, while the WE provides the interface electrode/electrolyte where the reaction happens;
- Current measurements: these are based on Kirchoff law using a virtual mass technique. The current on virtual mass pin is the same that flows through the Standard Resistor (RS) placed in the feedback ring. The consequent voltage is sent as input to the FRA.
- Voltage measurements: voltage is measured using a differential amplifier with high input impedance.

3) Measurements Methods: measurements methods adoptable to determine the electrochemical impedance are four:

- Measurements bridge: high precision but the measurements are long.
- Lissajous figures: allows measurements over a very broad frequency spectrum using an XY oscilloscope and a XY recorder.
- Contemporary tracing of Voltage and Current: a XY recorder can be used to analyze low frequency and very low frequency signal (f < 1Hz) contemporarily printing voltage and current. Their comparison allows to get module and phase of the impedance.
- Phase sensitive detection: using a lock-in amplifier is possible to detect the phase difference between the stimulus and output.

  Frequency Response Analyzer: the functioning block scheme is shown in Figure 4. A signal generator change its frequency from a minimum to a maximum value sending the signal versus the cell. The stimulus $x(t) = X_0 \sin \omega t$ is correlated with two synchronous reference signals, the first in phase with x(t) and the second 90° shifted (for example sin(ωt) and cos (ωt)):

$$Re = \frac{1}{T}\int_0^T S(t)\sin(\omega t)\,dt; \quad Im = \frac{1}{T}\int_0^T S(t)\cos(\omega t)\,dt$$

Where:

$$S(t) = X_0 K(\omega)\sin[\omega t + \phi(\omega)] + \sum_m A_m \sin[m\omega t - \phi_m] + n(t)$$

is the sum of the harmonics and of the noise for a cell having a transfer function equal to:

$$K(\omega)e^{j\phi(\omega)}$$

T is the integration time equal to the integer number of periods of the stimulus signal. The only integral different from zero is given by the fundamental the others, joined with the harmonics, are equal to zero. Considering an infinite integration time it is possible to get the following quantities:

$$Re = \lim_{T\to\infty}\frac{1}{T}\int_0^T S(t)\sin(\omega t)\,dt = X_0 K(\omega)\cos(\phi(\omega))$$

$$Im = \lim_{T\to\infty}\frac{1}{T}\int_0^T S(t)\cos(\omega t)\,dt = X_0 K(\omega)\sin(\phi(\omega))$$

Using this quantities, proportional respectively to the real and the imaginary part, it is possible to get the impedance.

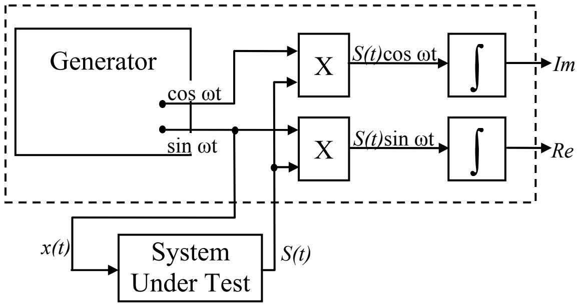


Figure 4. Frequency Response Analizer block scheme.

III. Market

At the moment, the market offers very good instrumentation to analyze the impedance of a fuel cell which can be directly measured by an impedance analyzer (IA) or through the combined action of a FRA and an ECI for little current (1÷2 A) or adding a booster for higher currents (up to 60 A) . This last provides to the cell under test the DC bias voltage or current which the FRA overlaps the ac stimulus. The FRA will pick up the signal coming from the DUT to get its impedance. The lasts interface allows to effect measurements on the cell with two, three or four terminals. Figure 5 shows the common hardware configuration to realize an electrochemical impedance measurement.

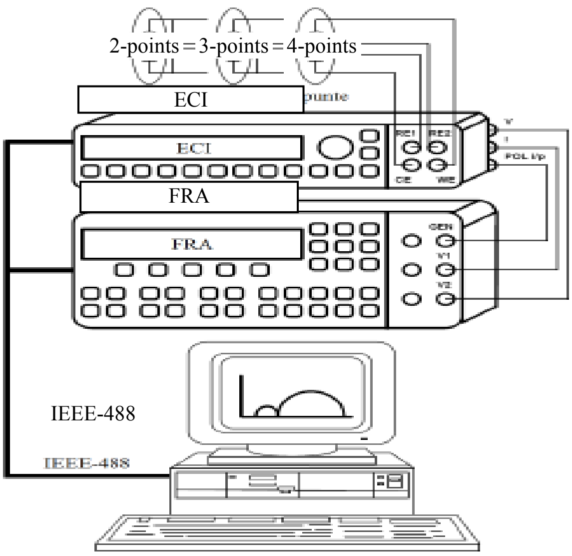


Figure 5. Frequency Response Analizer block scheme.

To effect measurement on high power electrochemical cell, the couple FRA-ECI needs of a power amplifier placed between the DUT and the electrochemical interface.

All products in the market have high precision but are very expensive and, being designed almost exclusively for research laboratory, they are multipurpose and non specialized for fuel cell.

Some models are for example:

- Solartron (FRA + ECI) with band pass from few µHz up to 32 Mhz and a current limit without booster of 2 A, with a cost of about 70,000 €.
- EG&G (FRA + ECI): device stand alone with band pass from few µHz up to 2 Mhz and a current limit without booster of 2 A, with a cost of about 30,000 €.

  Both, with booster, can arrive up to 60 A.

IV. Our Idea

The idea has been to realize a measurement setup for EIS analysis using an electronic load, a function generator and a personal computer without the use of instrumentation findable on the market. The idea is shown in figure 6.

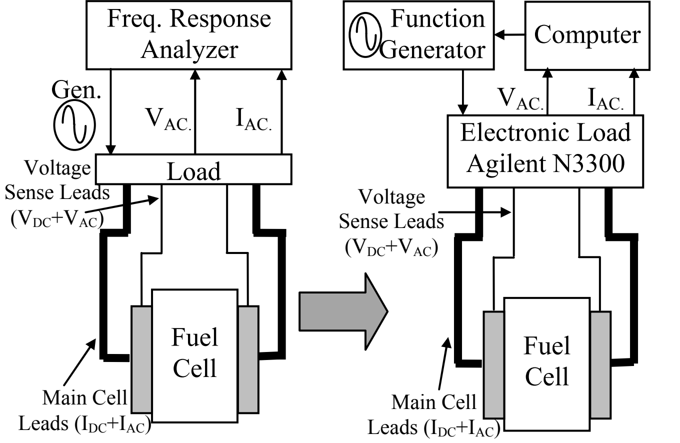


Figure 6. Our EIS system.

The core of the system is the electronic load which allows to simulate whatever resistance value the experiment needs, moreover can absorbs programmable current values from few mA to some tens of Amperes. Figure 7 shows the principle scheme of an electronic load.

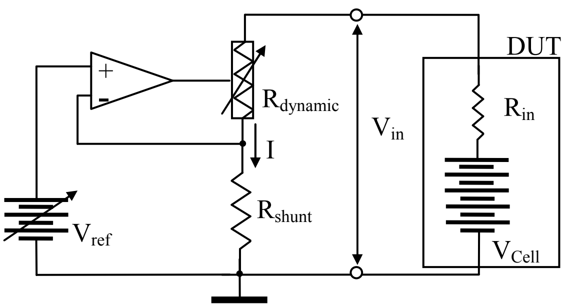


Figure 7. Principle scheme of electronic load.

The block *dynamic resistance* is composed by the parallel between strongly dissipating power transistors. The *shunt* is realized with a precise resistance with a defined value able to convert the current that flows in the dynamic resistance in a voltage. An operational amplifier controls the conduction of the transistors depending by the difference between the voltage on the shunt resistor and a reference voltage V_{ref} defined by the user. Depending $V_{ref,}$ the electronic load has three different functioning modes:

- Constant Current – if V_{ref} is constant, the system fixes a constant current equal to:

$$I = \frac{V_{ref}}{R_{shunt}};$$

- Constant Resistance - if V_{ref} varies in a way directly proportional with V_{in}, also the current I varies as the same. In this case the system works with constant resistance with value:

$$R = \frac{V_{in} R_{shunt}}{V_{ref}};$$

- Constant Power - if V_{ref} varies in a way inversely proportional to with V_{in}, also the current I varies as the same. In this case the system works with constant power with value:

$$P = \frac{V_{in} V_{ref}}{R_{shunt}};$$

A. *Agilent N3300A*

The Agilent N3300A[11] is the mainframe of electronic load used for designing, production and analysis of DC suppliers, batteries and power elements. The mainframe has six slots for the electronic load modules. Each one can dissipate up to 300 W for wholly 1800 W. The electronic load can be programmed by GPIB port through SCPI (Standard Command for Programable Instruments) commands or RS-232 port. In the mainframe used for the experiment there was a N3304A 60 V, 60 A, 300 W load module. The Agilent N3300A has three functioning mode:

- Constant Current (CC);
- Constant Voltage (CV);
- Constant Resistance (CR);

In the CC mode, the module will follow the current value previously fixed, independently by the input voltage. In the CV mode, the module controls the current in such a way that the source voltage is equal to that previously fixed. In the CR mode, the module controls the input current in a way directly proportional to the input voltage joined to the resistance value previously fixed. Both the current and the voltage can be programmed over two ranges the high (60 V, 60 A) and the low (6 V, 6 A) with higher resolution.

CC and CV mode can be managed by an external signal (AC or DC) which has to be connected to the programmable input. For a 0÷10V signal corresponds a variation 0 ÷ full scale both in CV and in CC.

During the test phase of the system, it has been observed that the ratio between the amplitude of the signal generated by the function generator and that provided by the electronic load did not respect the 1:1 ratio, but it decreases with the frequency of the signal. To face this problem a calibration procedure which give a calibration file has been realized. Using this file, the management program, knowing the operative frequency, can suitably increase the amplitude of the signal coming from the function generator, to get the right amplitude.

The range cost of the whole system including a commercial functions generators a PC and the Agilent N3330A mainframe, is 4,000÷5,000 € depending on the models chosen for the firsts two devices.

B. Software

LabView is the tool used to create the management program of the instrument which follows the flow chart of Figure 8 inspired to the work of Lo Presti *et al.* [14].

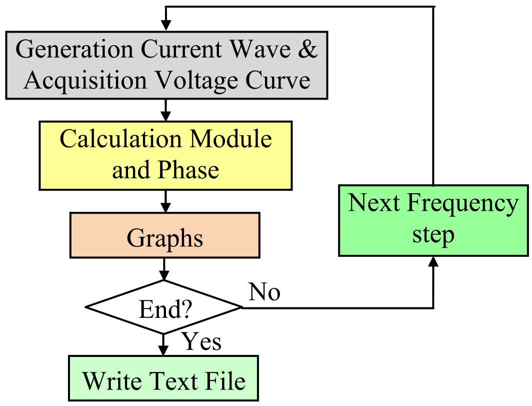


Figure 8. Flow Chart of the system control program.

AS the flow chart shows, for each frequency step the system provides to the DUT new current waves and simultaneously acquires voltage curves, then it calculates module and phase of the impedance. Moreover the program graphs the impedance and save data on a text file. It is possible to visualize acquired and calculated data in five different modes:

- *Data* – a five columns table is shown: the list of frequencies generated is shown in the first column, in the next four columns are shown the measurements and in particular the real part of the impedance, the imaginary part, module and phase on a Bode diagram.
- *Curve* – in this mode are shown both the current wave through the electronic load and the voltage picked up on it.
- *Nyquist* – module and phase on complex plane are shown by Nyquist graph.
- *Bode* – module and phase on complex plane are shown by Bode graph.
- *Real-Imm* – real and imaginary part of impedance function of frequency are graphed in this mode.

Figure 9 shows the *Curve* mode where current is drawn in green while the acquired voltage is in red.

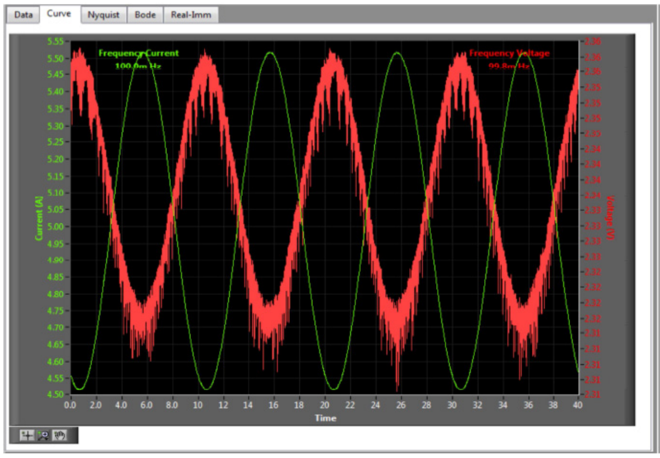


Figure 9. Curve mode window.

V. Characteristics of the Instrument

Currents and Voltages, input of the module, are constantly measured with a resolution of 16-bits. Power is obtained starting by Voltages and Currents measurements. The maximum power of the system is 300 W expandable up to 1800 W. All measurements are obtained digitalizing the instant value of the voltage and of the current for a precise number of samples which are then recorded in a buffer. It is possible to program the following measurement parameters:

- Number of samples (N);
- Time interval between samples (Δt)
- Trigger Mode.

The buffer dimension can be changed from 1 to 4096 samples, while the Δt can be changed from 10 µs up to 3200 µs with step of 10 µs. Known these parameters is possible to calculate the resolution, the maximum and minimum frequency that the mainframe is able to configure.

A. Dynamic Characteristics

To warranty that the software is able to build the sinusoidal signal with a minimum error margin, the time window for the sampling has to contain at least four sinusoids. It has been also evaluated that for a high fidelity sinusoid reconstruction, this has to be composed by at least 10 points.

To calculate the maximum frequency rebuilded by the system, it is necessary to determine the minimum sampling time window:

$$W_{min} = N_{min} \text{ x } \Delta t_{min} = 10 \text{ x } 0.00001 = 0.0001 \text{ s}$$

$$f_{max} = \frac{1}{W_{min}} = \frac{1}{0.0001} = 10 \text{ kHz}$$

The limit of the minimum frequency is joined to with the number of recordable samples. In this case the sampling time window has to be the most large possible:

$$W_{max} = N_{max} \times \Delta t_{max} = 4096 \times 0.032 = 131.072 \text{ s}$$

so the minimum frequency rebuilded by the system is:

$$f_{min} = \frac{1}{W_{max}} = \frac{1}{131.07} = 7.62\ mHz$$

The maximum resolution achievable by the instrument depends by the range of the adopted ratio voltage/current. For the 6 V range we have:

$$\Delta V = \frac{6}{2^{16}} = \frac{6}{65536} = 0{,}000091V = 91\ \mu V$$

while for the range of 60 V:

$$\Delta V = \frac{60}{2^{16}} = \frac{60}{65536} = 0{,}00091V = 910\ \mu V$$

Obviously for the current we obtain the same values:

$$\Delta I = \frac{6}{2^{16}} = \frac{6}{65536} = 91\ \mu A \text{ and } \Delta I = \frac{6}{2^{16}} = \frac{6}{65536} = 910\ \mu A$$

In the Table I are summarized the principal dynamic characteristics of the N3300A mainframe.

TABLE I. DYNAMI CHARACTERISTICS OF N3300A MAINFRAME

Frequency	f_{MAX} 10 kHz	f_{MIN} 7 mHz
Resolution Voltage Current	6V/6A 91 μV 91 μA	60V/60A 910 μV 910 μA

Even if the dynamic characteristics are generally lower than commercial multipurpose EIS instrumentations, they show as the device is particularly suitable for fuel cells investigations and moreover extremely cheaper.

VI. Calibration Test and Measurements

To validate the system, a lots of calibration have been effected on well known circuit giving us the expected results. An example is here presented. A circuit composed by a parallel between a resistance (0.5 Ω) and a capacitor (6 mF) has been realized and tested with our EIS system. Figure 10 shows the circuit which simulates a cell.

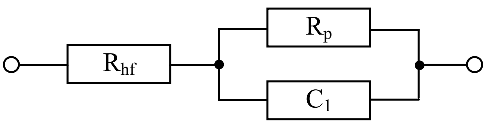


Figure 10. Circuit of simulated cell.

where R_{hf} is the resistance at high frequency, R_{lf} is the resistance at low frequency, $R_p=R_1$ is the polarization resistance difference between R_{lf} and R_{hf} , C_1 is the test capacitor. For this circuit the cut frequency (f_{-3dB}) is equal to 53.05 Hz. Next Figures show as the EIS system correctly detects this frequency.

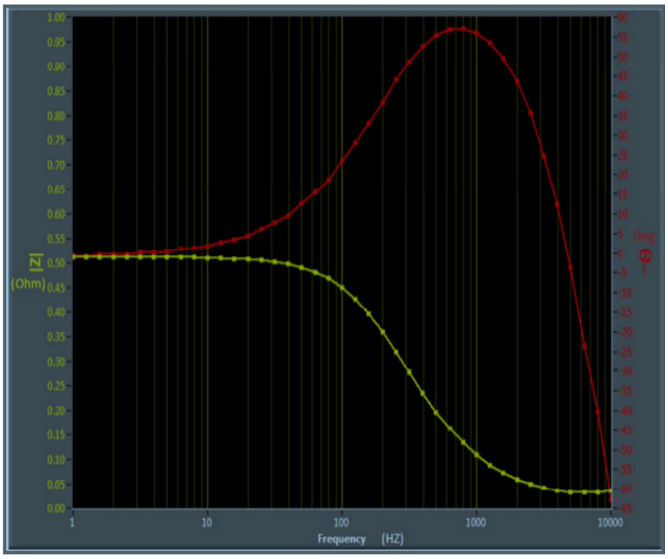


Figure 11. Bode graph of module and phase of the test circuit impedance.

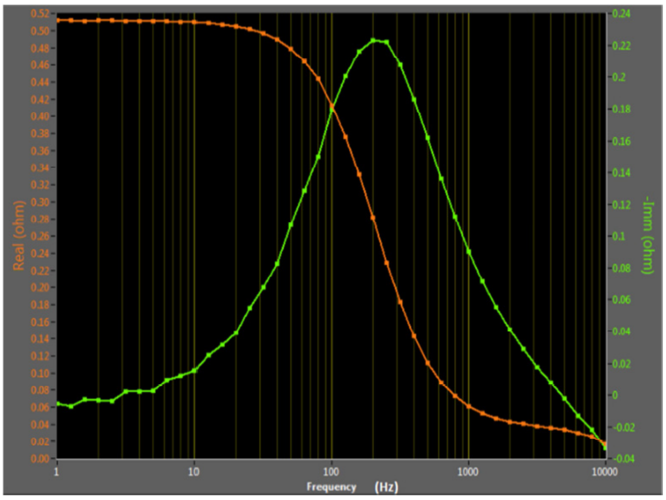


Figure 12. Real and imaginary part of impedance vs. frequency graph of the test circuit impedance.

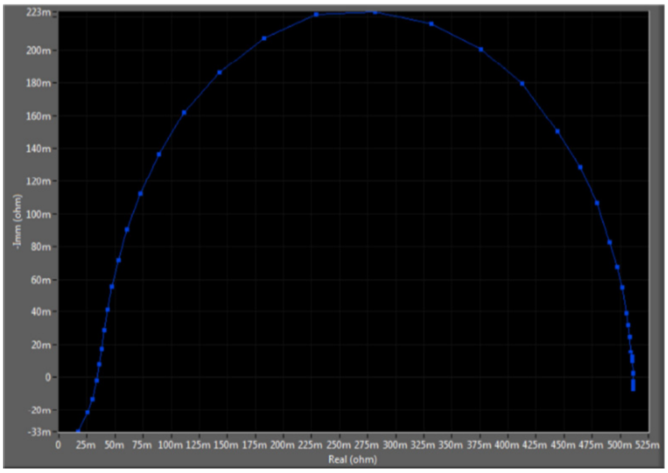


Figure 13. Nyquist graph of the test circuit impedance.

Next figure shows the behavior of the impedance spectrum for a NEXA stack. The diameter of the semicircle decreases for load current higher. The intercept with the real axis for all semicircles is always the same verifying that the R_{hf} is constant varying the load. On the contrary for low frequencies the interception between the different curves with the module axis is higher for load lower and this means that the resistance for low frequencies decreases for load higher.

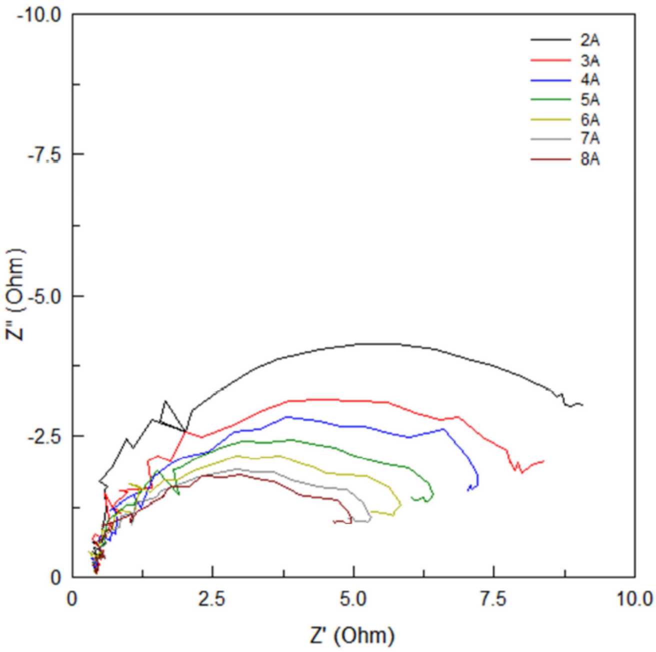


Figure 14. Nyquist graph of the NEXA stack impedance for 2, 3, 4, 5, 6, 7, and 8 A load currents.

Considering that the intercept with real axis for high frequency represents the electrolyte resistance while, the diameter of the semicircle represents the polarization resistance, it is clear from the figure that for higher current load the polarization resistance decreases, while the electrolyte resistance is constant.

VII. Conclusions

Exploiting commercial functions generators, common PCs and the Agilent Mainframe N3300A used as electronic load, a very useful and economic Electrochemical Impedance Spectroscopy Instruments has been realized. Although the performances of this device can not equal some commercial ones designed for multipurpose, for fuel cells analysis it shows performances equal to the best instruments on the market but it is extremely cheaper.

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