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Virtual impedance spectroscopy for electrolytical cells

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Abstract **-** Impedance spectroscopy play an important role in fundamental and applied electrochemistry and materials science. In a number of respects it is the method of choice for characterizing the electrical behavior of systems in which the overall system behavior is determined by a number of strongly coupled processes, each proceeding at a different frequency. The paper presents a virtual instrument and the associated hardware that allows to perform the impedance spectroscopy on an electrolytical cell. It is aimed for studying phenomena (charge transfer, difusion or electrode polarisation) that occur while growing nanowires in polycarbonate templates. The hardware consists of a NI PCI6111 data acquisition board and external analog front end (programmable current to voltage converter and programmable mixed voltage generator). The software is developed in Labview and allows to perform the impedance spectroscopy and to save the data on a file. With a different software, the system can be used also for electrochemical deposition or for etching of the polymer membranes with ion tracks. Detailed schematic description is presented, together with experimental results.

I. Introduction

As it is known, impedance spectroscopy means the evaluation of impedance behavior of a physical system in a wide frequency range by applying a single frequency voltage and measuring the current flowing through it.

Considering a sinus wave signal as voltage

$$v(t) = V_m \sin(\omega t) \tag{1}$$

applied to a system, the current response

$$i(t) = I_m \sin(\omega t - \varphi) \tag{2}$$

of this system can be measured. Following, the impedance of the system can be calculated as [1]:

$$Z(t) = \frac{u(t)}{i(t)} = \frac{U_m \sin(\omega t)}{I_m \sin(\omega t - \varphi)} = Z_m \frac{\sin(\omega t)}{\sin(\omega t - \varphi)} \tag{3}$$

In complex it will be

$$\underline{Z} = \frac{\underline{U}}{\underline{I}} = \frac{|\underline{U}| \cdot e^{j\omega t}}{|\underline{I}| \cdot e^{j(\omega t - \varphi)}} = |\underline{Z}| \cdot e^{j\varphi} = |\underline{Z}| \cdot (\cos\varphi + j\sin\varphi) \tag{4}$$

The impedance can be plotted in the plane in either rectangular

$$\begin{cases} \mathrm{Re}(\underline{Z}) = Z' = |\underline{Z}|\cos\varphi \\ \mathrm{Im}(\underline{Z}) = Z'' = |\underline{Z}|\sin\varphi \end{cases} \tag{5}$$

or polar coordinates

$$\begin{cases} |Z| = \sqrt{(Z')^2 + (Z'')^2} \\ \varphi = arctg\,\dfrac{Z''}{Z'} \end{cases} \tag{6}$$

(see Figure 1).

Impedance Spectroscopy (IS) is a useful electrochemical tool for characterizing intrinsic electrical properties of any material or its interface. The basis of IS is the analysis of the impedance of the system versus the frequency of the applied signal. It provides quantitative information about the conductance,

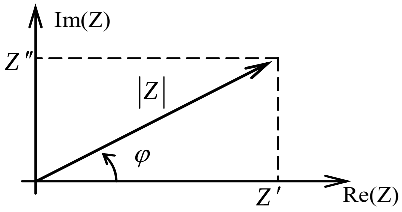


Figure 1. Impedance representation in the plane.

the dielectric coefficients, the static properties of the interfaces of a system, and its dynamic change due to adsorption or charge-transfer-phenomena. IS uses sinus signals with low amplitude. This allows a non-invasive observation of the test sample without any or with less influence of the electrochemical state. There are commercially available, high-quality impedance bridges and automatic measuring equipment covering from millihertz to megahertz frequency range. It emerges that the impedance studies became more popular for many electrochemists, materials scientists, and engineers for understanding the physical phenomena and for the interpretation of the impedance data.

IS is a necessary analytical tool in materials research because it involves a relatively simple electrical measurement that can be automated and whose results may often be correlated with other complex materials variables, like mass transport, rates of chemical reactions, corrosion and dielectric properties, or defects, microstructure and compositional influences on the conductance of solids. IS can mark out aspects of the performance of chemical sensors and it has been used extensively to investigate membrane behavior in living cells or in electrodeposition processes. It is also useful as an empirical quality control procedure. IS has an equally important area of application in the study of materials that are not intended for electrical applications, for example, structural ceramics, in which transport properties are incidental to the main application.

The advantages of impedance measurement over other techniques include: rapid data acquisition (minutes), accurate measurements, non-destructiveness, highly adaptability to a wide variety of applications.

The disadvantages of IS are primarily associated with possible ambiguities in interpretation.

If the real part of impedance is plotted in the plane on the X axis and the imaginary part on the Y axis, we get a "Nyquist plot". Figure 2 shows two RC circuits common in impedance spectroscopy and typical Z complex plane response for them.

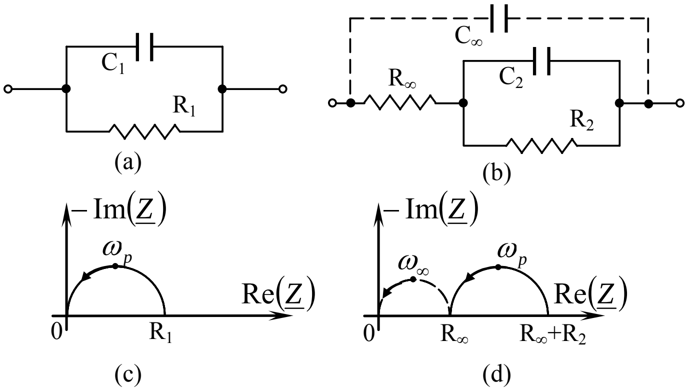


Figure 2. a), b) – two common RC circuits; c), d) – their impedance plane plot. The arrows indicate the direction of increasing frequency.

Analysis of experimental data that showing a full semicircular arc in the complex plane, such as in figure 2(c), provides estimates of the parameters R_1 and C_1 and hence, lead to quantitative estimates of conductivity, faradic response rates, relaxation times, and interfacial capacitance.

II. Electrolytic cell

The system presented in this paper is aimed for performing impedance spectroscopy on an electrolytical deposition cell. A few tenth µm thick polycarbonate membrane with a single heavy ion track (11.3 MeV/u U_{238}, is inserted into an electrolytic cell consisting of two cell halves with flat sealing surfaces facing the central membrane (Figure 3, [2,3]).

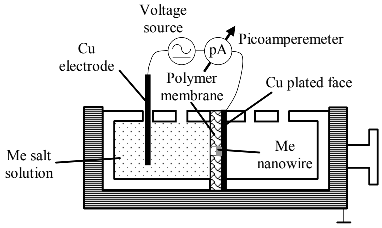


Fig. 3

The membrane is previously etched until the nanohole reach the desired diameter [xx]. Second, a copper layer is electroplated on one face of the membrane, having the role of electrode in the process of electrodeposition. A second electrode is inserted in the solution containing the ions of the metal (Me) to be deposited. As long as the nanohole is not filled, the solution will reach the Cu back plane. Applying a voltage, larger than the electrochemical potential of the metal to be deposited, the nanohole will be filled, starting from the backplane with metal. The resulting nanowire has a crystalline structure. The structure depends on the solution parameters and on the applied voltage. Here comes the importance of performing the impedance spectroscopy on the cell. Usually the impedance varies from very high (1000MΩ) to normal values (200Ω). The maximum current that a nanowire can stand is around 1 mA, but while growing it will rise from pA to tenth of nA [4].

Impedance spectroscopy on the electrolytical cell must be performed at the working potential in order to get the right information. Thus, a sinus wave much smaller than the working potential must be applied on top of it with the frequency varying from mHz to 100kHz. Usual electrochemical potentials stand under 1V the sinus wave must have at least 10 times smaller amplitude. This will reflect in 10 times smaller current.

III. Hardware description

The hardware is built around a high speed data acquisition board (NI PCI6111). It has been chosen because high frequencies (up to 100kHz) are necessary for observing charge transfer phenomena while the DAQ card allows sampling frequency up to 4MS/s and output update rate up to 2Ms/s and because of the high output resolution (16 bits) [5]. The hardware is completed with analog front end and digital buffers for driving input and output scales. The block diagram is presented in Figure 4.

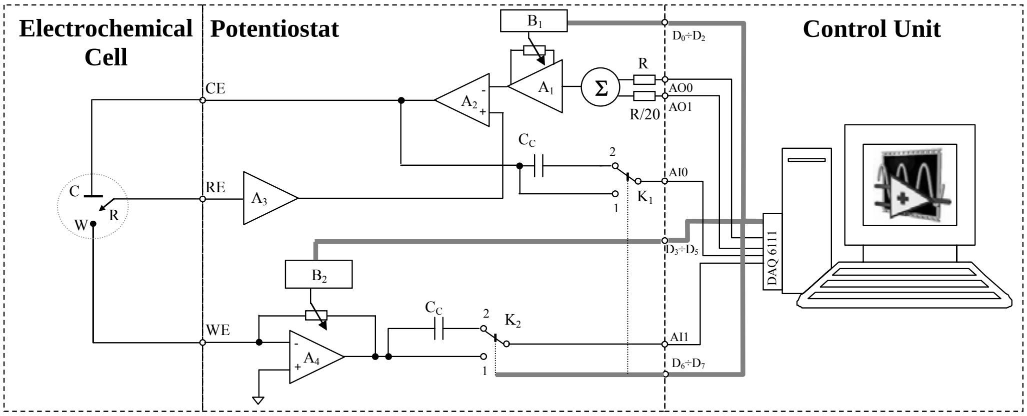


Figure 4 The block diagram of the impedance spectrometer

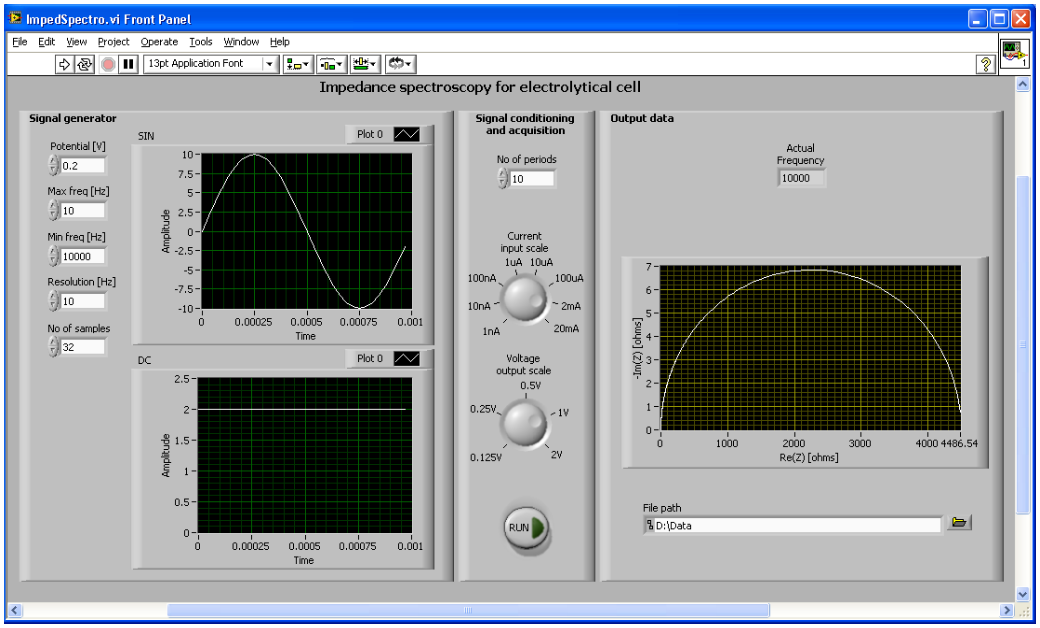
For generating the DC potential and the sinus wave superposed on it we need both analog outputs: AO_0 for the DC potential and AO_1 for the sinus wave. Both will be generated with maximum of resolution (16 bits, full scale). Next the two voltages are weighted summed (Σ) in order to get a 20 times smaller sinus than the DC potential. The sinus wave is attenuated together with the DC wave when the operator change the DC range ($D_0 \div D_2$). Five ranges are available: 2V, 1V, 0.5V, 0.25V and 0.125V. Thus, the ratio between them remains 20, no matter which is the DC potential. Because in electrochemistry electrodes must be referred to some reference potential, the amplifier A_3 is buffering the voltage given by a reference electrode inserted in the cell also. The amplifier A_2 is subtracting the reference voltage from the generated one. This way, the potential between the counter and the working electrode will be the prescribed voltage from the front panel of the virtual instrument. The applied voltage on the counter electrode is then read using the analog input AI_0 in order to calculate the impedance. Because the signal carrying the information is the sinus, and its amplitude is reduced (100mV amplitude for 2 V DC), it is extracted with a capacitor (C_C and K_1) and it is amplified with the data acquisition input amplifier (the gain for channel 0 is set up to 20).

The current flowing through the cell is measured with the picoamperemeter realised with the stage A_4 (LMC6001 [6]). Its conversion ratio is programmable using the digital lines $D_3 \div D_5$ of the DAQ card. There are 8 ranges available for current: 20mA, 2mA, 200μA, 20μA, 2μA, 2000nA, 20nA, 2nA. The measured current contains also, the DC component and the sinus component which is 20 times smaller. The scale cannot be changed because the DC component will bring it into saturation. Therefore, the sinus is separated and the gain of the input amplifier from the data acquisition board will be fixed to get the optimal resolution.

The system can work also as potentiostat too, by keeping to zero the sinus wave amplitude, and switching K_1 and K_2 on position 1.

IV. Software description

The software is realised in LabView 8.2. The front panel is shown in figure 5.



Potential [V] 0.2

Max freq [Hz] 10

Min freq [Hz] 10000

Resolution [Hz] 10

No of samples 32

No of periods 10

Actual Frequency 10000

File path D:\Data

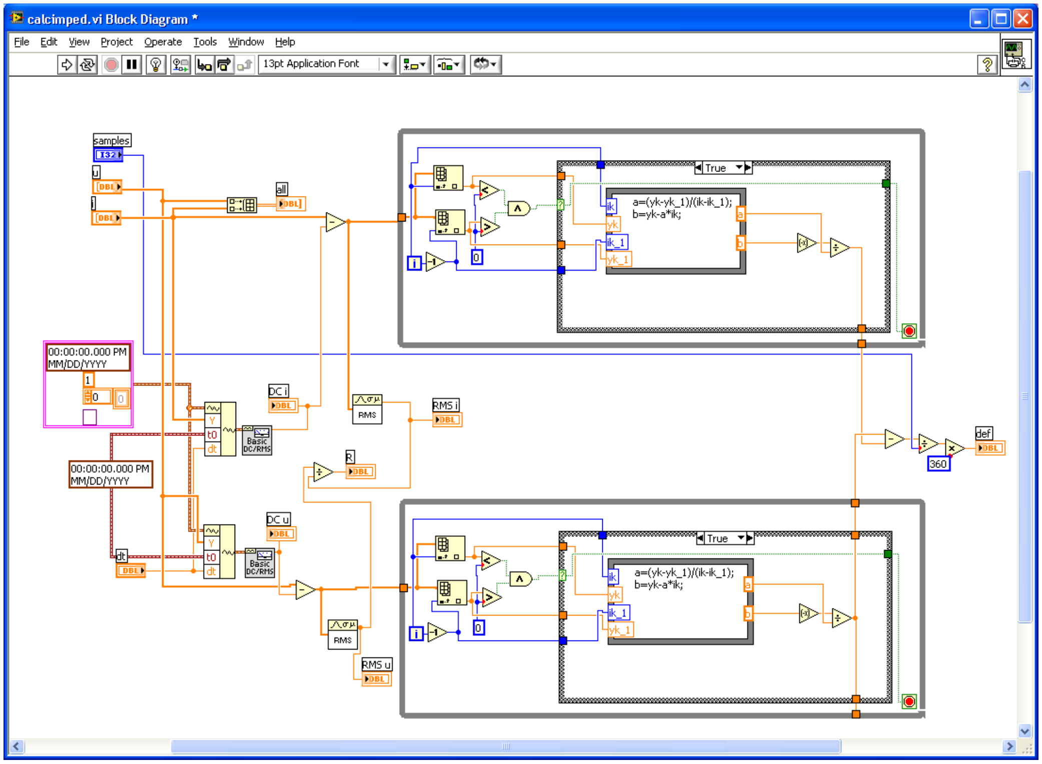
Figure 5 The front panel of the virtual instrument

The operator has the signal generator in the left part. The DC voltage and the frequency limits, together with the resolution and the number of samples can be pre-programmed. In the middle the operator can choose the voltage output scale and the current range. Also, the number of periods to be analysed is also available. Once the parameters chosen, the button Run must be pressed.

In the right side output data is displayed –Im(Z) function of Re(Z). Data is saved in a file; location can be chosen from front panel.

The process starts applying the DC potential and the sinus wave when the "Run" button is pressed. The frequency is incremented, according with the resolution programmed, on each step. For each frequency the specified number of periods ("No of periods" controller) are analysed and the result is averaged for better accuracy. After the high frequency limit is reached the process is stopped, the full graph is available, and also the data file will be closed.

The main part is the VI performing the impedance computation (Figure 6). It calculates the impedance from the delay between the voltage and the current wave. For this, it calculates the fractional indexes for the passages through zero of the two waves. Because the VI available in LabView is not working properly if the threshold is smaller than the first element: “This function does not recognize the index of a negative slope crossing, and it might return incorrect data if **threshold y** is less than the value at **start index**.”, another algorithm has been used. It finds the first pair of consecutive samples, first below and second above zero. When this happens it calculates the fractional index. Subtracting the indexes for the two waves and multiplying with the sampling period, the time delay can be computed. Dividing it to the signal period (measured between two consecutive zero passages) the phase shift angle is computed. The method shows a good accuracy for the measured angle (below 0.1 degree), even for low number of samples per period.



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a=(yk-yk_1)/(ik-ik_1);
b=yk-a*ik;
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```
a=(yk-yk_1)/(ik-ik_1);
b=yk-a*ik;
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Figure 6 Phase shift measurement VI

V. Conclusions

The paper presented a virtual impedance spectrometer for electrochemical cell. It allows measuring the impedance over a large frequency range (mHz to 100kHz). It consists of a hardware front end attached to data acquisition board (NI PCI6111), that allows applying the working DC potential and a small sinus wave on top of it, and to measure both, the applied voltage and the current flowing through the cell from pA range up to mA. The operator has to fix only the DC potential, while the hardware will fix the sinus is always 20 times smaller than it. The system is simple and versatile (can perform impedance spectroscopy or it can be used for etching the polymer membranes and for growing nanowires), has low cost, it is connected to the computer, it can operate for long time without slowing down the host computer, the measured data being saved periodically on the hard disk. Later, data is available in spreadsheet file format for post-processing.

The picoamperemeter has been calibrated using a Keithley 6487 sourcemeter. Errors and results were presented in a previous paper [7]. In Figure 7 is shown an impedance spectroscopy performed on the electrochemical cell filled with CdTe solution in a frequency range from 0.1Hz up to 100kHz. The physical model is the same as the one presented in Figure 2 a, a simple parallel RC circuit. We can note that R_1 is around 530 ohms and ω_p is the parallel resonant frequency that is around 14 kHz. Such equivalent schematic can say that the response is associated with a heterogeneous electrode reaction. The value C_1 that can be extracted from the resonant frequency is the diffuse double layer capacitance of the polarization region near the electrode in simplest cases. Electrochemist can use this information for adjusting the solution or the entire setup.

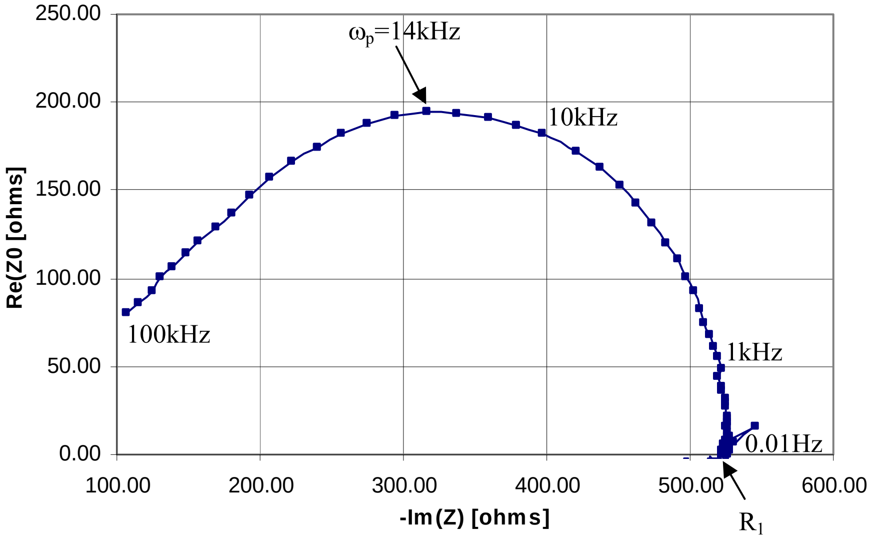

Figure 7 Impedance spectroscopy data for electrochemical cell filled with CdTe solution

Acknowledgement

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