International Journal of Engineering Research and General Science Volume 3, Issue 4, July-August, 2015
ISSN 2091-2730

Impedance Spectroscopy of Tap or Raw Water in 1 MHz to 10 MHz Range

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Abstract— Impedance spectroscopy of raw or tap water sample derives from the measurement of the current into and the voltage across the water sample as function of applied linear frequency modulated signal in 1 to 10 MHz frequency range. It is the method to measure real impedance and imaginary impedance of water components. The impedance of the sample can be calculated by applying linear FM wave to the water sample input in series with a known resistor and measuring voltage across the resistor. Performing this measurement by changing the frequencies of the applied signal provides the impedance phase and magnitude. The complex impedance is then calculated and data obtained from measurement are fitted into LEVM program with appropriate model. Then parameters are extracted to describe the electrical properties of the water sample.

Keywords— Spectroscopy, Linear FM wave, LEVM, EIS

INTRODUCTION

Impedance spectroscopy is a method of characterizing the electrical properties of material and their interfaces with electronically conducting electrodes. It is used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic semiconducting, mixed electronic-ionic and even insulators (dielectrics). Electrical measurements to evaluate the electrochemical behavior of electrode and electrolyte material are made with cell having two identical electrodes applied to the faces of a sample in the form of circular cylinder or rectangular parallelepiped. The general approach is to apply and electrical stimulus (a known voltage or current) to the electrodes and observe the response (the resulting current or voltage). The efficiency of this method relies on the possibility to get information in three dimensions: the real and imaginary part of the impedance and the frequency. The general approach in Electrical Impedance Spectroscopy (EIS) is to apply an electrical stimulus (a known voltage or current) to the material and then to observe the resulting current or voltage as shown in figure 1.

The stimulus can be applied in many forms. Macdonald (1987) gives three possible forms:

I. Step function: a step voltage $v(t)$ is applied at $t=0$ to the material and a time varying current $i(t)$ is measured. It is then Fourier-transformed into the frequency domain in order to calculate the frequency-dependent impedance.
II. Noise signal: a continuous voltage composed of random noise with energy over a known frequency range is applied to the material and the resulting current is measured and then Fourier-transformed into the frequency domain.
III. Sinusoidal signal: a multi-frequency voltage or current is applied to the material and the resulting frequency-dependent current or voltage is measured. The response is measured in the frequency range of interest in terms of either phase shift or amplitude or real and imaginary parts.

The research described in this is concerned with EIS using the sinusoidal stimulus approach with varying frequency in linear mode called linear frequency modulation or chirp signal. A multi-frequency current is applied to the material and the resultant voltage is measured. It has to be emphasized that the material is always assumed to have time-invariant properties. Also, it is assumed that the material is electrically linear, which means that the reciprocity theorem can be applied. The points of current injection and potential measurement can be interchanged without changing the ratio of voltage to current.

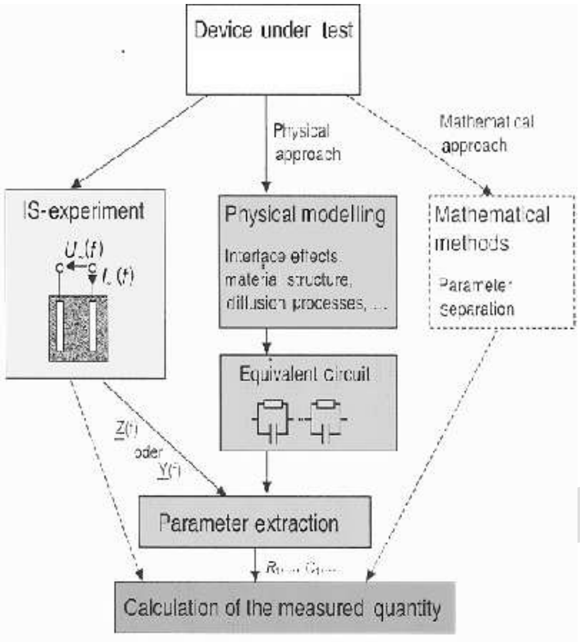


Figure 1 Impedance spectroscopy [1]

Background of Electrolyte impedance

Water exhibits the properties of both conductors and dielectrics, i.e. they contain both free and bound (fixed) charges. As a result water impedance contains both conducting and dielectric terms. The conductivity term (σ) accounts for the movement of free charges and the relative permittivity term ($\varepsilon\ r$) accounts for the movement of bound charges in the dielectric due to an applied electrical field. Water in cell having two electrode of area A and distance d may have conductivity σ and relative permittivity ε_r as shown in figure 2a. A model consisting of a resistance in parallel with a capacitance as shown the figure 2b can represent the electrical properties of water. However, this model cannot explain the whole of water properties over a wide range of frequencies. Dielectrics consist of polar molecules, or non-polar molecules, or very often both. Due to the asymmetric configuration of polar molecules, material consisting of these molecules has built-in dipole moments. Under an external electric field, the polarized dipoles reorient in the electric field and neutralize some of the charges on the electrodes. The most often used measure of material dielectric properties is the complex dielectric permittivity. It is a measure of the ability of the dielectric material to reorient and neutralize charges on the electrodes. Sometimes, relative complex dielectric permittivity is used to describe material dielectric properties. It is defined as the ratio between the dielectric permittivity of the material and that of free space. The dielectric permittivity of free space is $8.85\times10^{-12}\ F/m$.

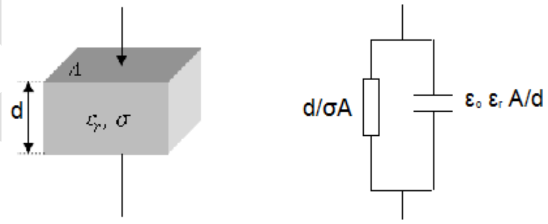


Figure 2 (a) Idealized bulk Electrolyte, where A is the area, d is the distance, ε_r is the relative Permittivity and σ is the conductivity. (b) Equivalent circuit of the water represented by a resistance in parallel with a capacitance, where ε_o is the permittivity of free space (8.85×10^{-12} F/m).

The dielectric permittivity of most dielectric materials is frequency-dependent. In the presence of an alternating electric field, the dipole moments inside the material oscillate with the direction of the electric field. The higher the frequency the harder it is for the dipole moments to catch up with the change of field direction. This results in a decreasing ability of the material to neutralize charges on the electrodes at high frequencies. In general, the total complex dielectric permittivity $\varepsilon^*(\omega)$ is written as:

$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ where ε' and ε'' are, respectively, the real permittivity and the dielectric loss factor of the material. ω is the angular frequency in radians.

Impedance measurement method

There are many measurement methods to choose from when measuring impedance, each of which has advantages and disadvantages. There are six commonly used impedance measurement methods, from low frequencies up to the microwave region and its advantages and disadvantages of each measurement method. The choice of the method is depended on the various factors like frequency coverage, measurement range, measurement accuracy, and ease of operation. Considering only measurement accuracy and ease of operation, the auto-balancing bridge method is the best choice for measurements up to 110 MHz. For measurements from 100 MHz to 3 GHz, the RF I-V method has the best measurement capability, and from 3 GHz and up the network analysis is the recommended technique.

The auto-balancing bridge method is commonly used in modern LF impedance measurement instruments. Its operational frequency range has been extended up to 110 MHz. Basically, in order to measure the complex impedance of the DUT (Device Under Test) ,it is necessary to measure the voltage of the test signal applied to the DUT and the current that flows through it. Accordingly, the complex impedance of the DUT can be measured with a measurement circuit consisting of a signal source, a voltmeter, and an ammeter as shown in Figure 3. The voltmeter and ammeter measure the vectors (magnitude and phase angle) of the signal voltage and current, respectively.

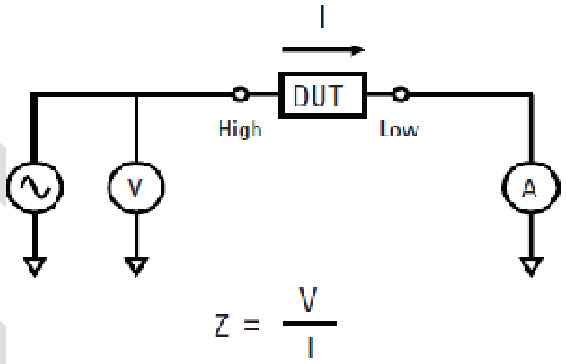


Figure 3 Simple model for impedance measurement [2]

There are different methods available for measurement of impedance. The data i.e. frequency and impedance (real and imaginary part) can be determined by the output measurement from DPO. From this data the value of R and C of the equivalent circuit of water can be find using complex nonlinear least square (CNLS) method in LEVM software.

Data analysis method:

The water sample (electrolyte) interfaced with electrode is considered as an equivalent circuit consisting of resistor and capacitor as an element. Many different equivalent circuits have been proposed but no one circuit structure is appropriate for all situations. Figure 4 shows a circuit, however, that has been found useful for a variety of materials and experimental conditions. Cg, the geometrical capacitance, and R, the high-frequency limiting resistance, represent bulk properties. C_R, associated with an electrode reaction, is the double-layer capacitance (possibly including both a compact inner-layer capacitance and a diffuse double-layer capacitance), and R_R is the reaction resistance. Finally, C_A and R_A are associated with adsorption at an electrode. The ZD elements, when present, are distribute circuit element (DCE)s. Bulk resistance and capacitance are extensive quantities, dependent on the effective separation between electrodes.

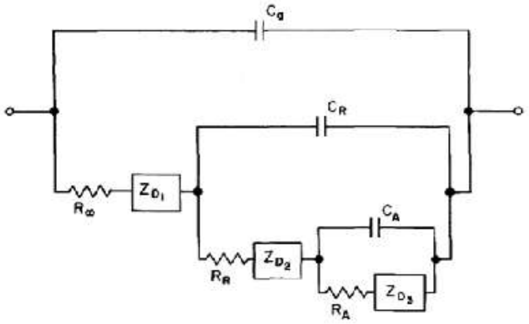
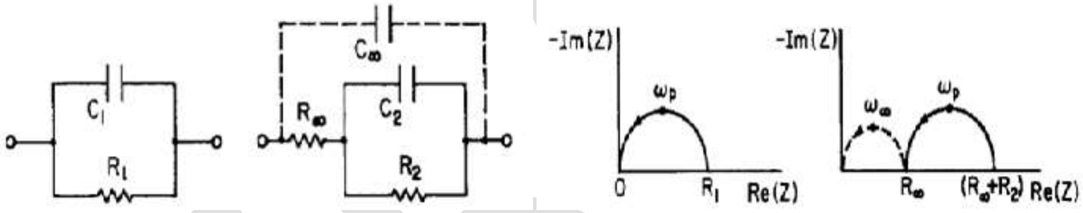


Figure 4 an equivalent circuit of hierarchical structure useful in fitting much IS data. [3]

Figure 5 shows two RC circuits common in IS and typical *Z complex* plane responses for them. The response of Figure 4(a) is often present (if not always measured) in IS results for solids and liquids. Any electrode–material system in a measuring cell has a geometrical capacitance *Cg*= *C* = *C*1 and a bulk resistance *Rb*= *R* = *R*1 in parallel with it.



(a) *(c)* *(b)* *(d)*

Figure 5 (a) and (c) show two common RC circuits. Parts (b) and (d) show their impedance plane plots. Arrows indicate the direction of increasing frequency. [3]

When non-overlapping semicircular arcs appear in, say, the impedance plane, one can directly estimate the associated *R* and *C* values from the left and right intercepts of the arc with the real axis and the value of w at the peak of the arc, $\omega = 1/(RC)$. This procedure is quite adequate for initial estimates, but it yields no uncertainty measures for the parameters and does not check that the frequency response along the arc is consonant with that for an *R* and *C* in parallel. Further, experimental arcs rarely approximate exact semicircles well.

Complex Nonlinear Least Squares (CNLS):

Simple method does not use all the data simultaneously, and they are often restricted to the analysis of limited situations (e.g. two possibly overlapping arcs). Nevertheless, when applicable, these methods are useful for initial exploration of the data and for initial parameter estimates for use in CNLS fitting. Complex nonlinear least squares avoids most of the weaknesses of earlier methods since it fits all the data simultaneously and thus yields parameter estimates associated with all, rather than half, the data. In addition, it provides uncertainty estimates for all estimated parameters, showing which ones are important and which unimportant in the model or equivalent circuit used for fitting; and finally, it allows one to fit a very complex model, one having 5, 10, or even more unknown (free) parameters.

Overview of LEVM program:

The LEVM program includes four main functions. First, it may be used to fit frequency-response or transient-response data by complex nonlinear least squares (CNLS) or nonlinear least squares (NLS). It may also be used for simulation of circuit and other model response functions. All output results may be plotted in 2- or 3-D form at any immittance level. When data are input into LEVM, the form of the data (i.e. impedance, admittance, etc.) as they appear in the input file can be altered by an input choice so that the actual fitting will be carried out at any of the four-immittance levels. Fitting can be carried out for data in either polar or rectangular form. All data transformations and fitting types are possible. LEVM allows the direct nonlinear least squares (NLS) fitting of real or imaginary parts of a data set separately as well as combined (CNLS). LEVM.EXE can accommodate up to 2002 data points (1001 real and 1001 imaginary components) and up to 42 free parameters.

SIMULATION AND RESULTS

The simulation result in MATLAB of simple parallel RC circuit having different values of R and C is shown and the complex plane plots for different values of R and C in 500 KHz to 10 MHz frequency range are shown in figure 6. The water sample (electrolyte) interfaced with electrode is considered as an equivalent circuit consisting of resistor and capacitor as an element. The electrodes were prepared from copper metal in cylindrical form having diameter of 1 mm. The linear FM wave is applied to the water sample through coaxial cable. The frequency range of linear FM wave is 500 KHz to 10MHz with step frequency of 250 KHz. The input and output signal.

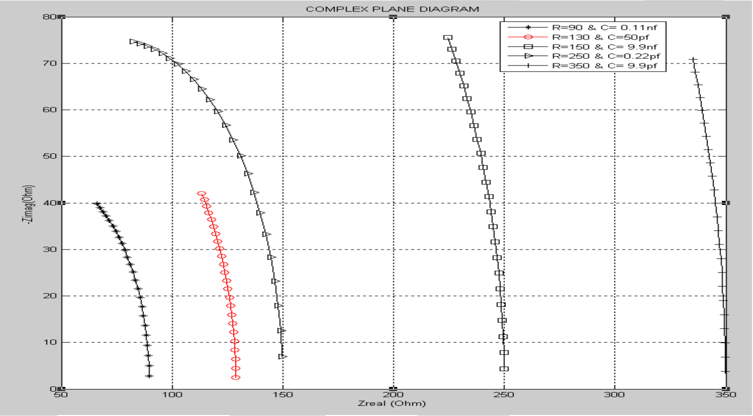
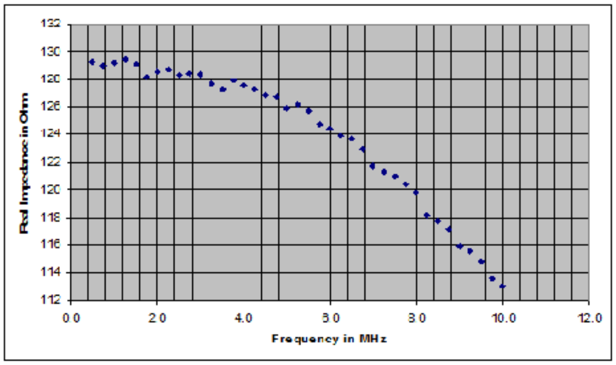


Figure 6 Simulation results in MATLAB

The water sample (electrolyte) interfaced with electrode is considered as an equivalent circuit consisting of resistor and capacitor as an element. The electrodes were prepared from copper metal in cylindrical form having diameter of 1 mm. The linear FM wave is applied to the water sample through coaxial cable. The frequency range of linear FM wave is 500 KHz to 10MHz with step frequency of 250 KHz. The input and output signal.

Figure 7 and 8 shows the real impedance and phase angle measurement of sample at various frequencies. The impedance spectrum obtained for water system is shown in figure 9. Investigation of the response shows that the plot is semicircular as the frequency increases.



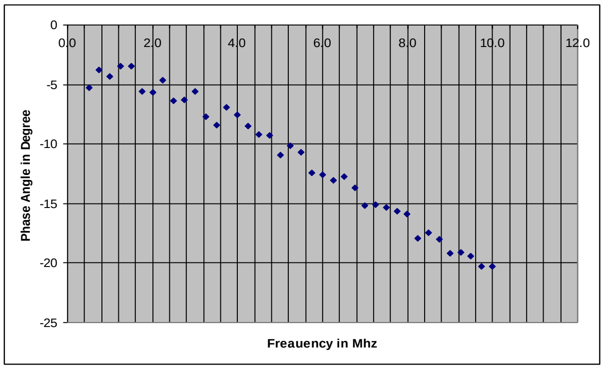


Figure 7 Real Impedance of water sample (Bode plot)

Figure 8 phase angle measurement of sample

The experimental data are fitted in LEVM –CNLS program and plotted in figure 8. The frequency dependence of the impedance of the simple R C parallel circuit with series resistor as it is displayed on a Bode plot (figure 7 and 8) and on a Nyquist plot (figure 9). A resistor's impedance does not change with frequency and that a capacitor's impedance is inversely proportional to the frequency. At very low frequency, the impedance of a capacitor is nearly infinite. The capacitance acts as if it were not there; it acts like an open circuit. Only the resistor remains present. It means that all of the current that passes through resistor. On the Bode plot the magnitude should be the value of resistor and the line should be horizontal. The phase angle should also be 0°. We see this "resistive" behavior at the low frequency (right) side of the Bode plot. At high frequency, the impedance also shows resistive behavior, but for a different reason.

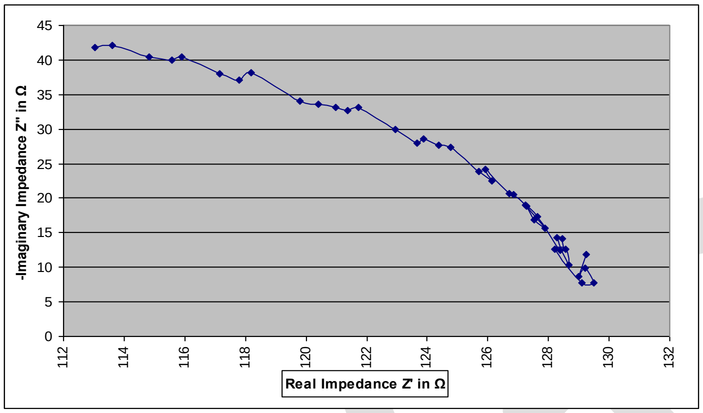


Figure 9 Complex Impedance response in Nyquist plot for water sample

As the frequency increases, the impedance of a capacitor becomes ever smaller. At some frequency, the impedance of the capacitor is so much smaller than R that all the current flows through the capacitor and none flow through R. At the limit of high frequency, the capacitor acts as if it were a short circuit, as a zero ohm impedance, or as a piece of wire. The impedance, then, is only the impedance of zero. This leads to the resistive behavior at the high frequency (left) end of the Bode plot. At intermediate frequencies, the capacitor cannot be ignored. It contributes strongly to the overall magnitude of the impedance.

CONCLUSION

The impedance spectroscopy measurement of water system was carried out in the 210 mv to 230 mv rms value and the frequency range was 500KHz to 10 MHz Simulation of the experimental impedance plots (Bode and Nyquist) is done using Complex Non-linear least square fitting program (LEVM)[5] and the best fit parameters (circuit elements) are obtained from analysis. The equivalent circuit that represented water system is best with two constant phase element. One of these constant phase elements was found to be a pure capacitor. This capacitor resulted from the parallel arrangement of electrode and having water in between the electrodes. The second constant phase element resulted from the resistance of charge transfer at the interface.

In present work, impedance data is collected for the frequency range 0.5 MHz to 10 MHz The frequency range can be extended up to 100 MHz or may be up to 1 GHz. Different impedance measuring technique is used for frequency above 100 MHz The distance between two electrodes and/or diameter of electrode can be changed. Different water sample like distilled water, pure water or sea water can be used. The observation of the impedance of water can be taken at different temperature as the permittivity of water is depended on the temperature. Similarly, the salinity is also important factor that can change the permittivity of the sample.

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