Electrical Impedance Spectroscopy – a powerful tool to characterize materials and physical processes

1 Introductive notions

The method of Electrical Impedance Spectroscopy (EIS) was described in details in many scientific books and articles[1]. Here we just notify that when a sample is subjected to an alternating electrical excitation (e.g. an electrical field generated by an applied alternating voltage $U(t) = U_0 e^{j(\omega t + \varphi_1)}$) its response, generally measured by the current $I(t) = I_0 e^{j(\omega t + \varphi_2)}$) that passes through the sample, is the *electrical impedance, Z*. This is defined as the ratio between the applied voltage and the resulted electrical current and is described as a phasor (complex number, usually expressed in exponential and/or trigonometrical form:

$$Z = \frac{U_0}{I_0} e^{j(\varphi_1 - \varphi_2)} = |Z| \cdot e^{j\theta} = |Z| \cdot (\cos\theta + j \cdot \sin\theta) \quad (1)$$

with $j = \sqrt{-1}$, $\theta = \varphi_1 - \varphi_2$ and $|Z| = \frac{U_0}{I_0}$.

When the phase θ between voltage and current is zero, the circuit is completely resistive (conductive); otherwise it is called reactive. The latter can be capacitive, when $\theta<0$, or inductive, when $\theta>0$. We note that a pure capacitive circuit is characterized by $\theta=-90^0$, a pure inductive circuit has $\theta=90^0$ and, of course, a pure resistive circuit yields $\theta=0$.

A complex sample will have this important parameter somewhere between these extremes. It is important for applications to understand the character of the sample; this is way the measured impedance is simulated by simple electrical circuits of resistors, capacitors and/or inductances. It is interesting to mention that, mathematically, the same value for the modulus, |Z|, and the argument, argZ=θ, of the impedance can be obtained by connecting the discrete elements of circuit in series and/or parallel. Finding the right approach is the privilege of the physicist looking at the results through the theoretical understanding and the direct application.

A simple tip is to identify the frequency dependency of the modulus and respectively the impedance argument. Considering the theoretical expressions, the *Table 1* is helpful to assign the best representation. Due to specificity of our measured samples, only resistor and capacitor circuits were considered. The variation sense is determined for the situation when the frequency increases.

Table 1.Variations of the impedance modulus and argument for series respectively parallel circuits of resistor and capacitor.

	series	**ω** ⇧	parallel	**ω** ⇧
|Z|	$\sqrt{[R_S^2 + 1/(\omega^2 \cdot C_S^2)]}$	⇩⇔	$R_P/\sqrt{1 + \omega^2 \cdot R_P^2 \cdot C_P^2}$	⇩
arg Z	$1/(\omega \cdot R_S \cdot C_S)$	⇩	$\omega \cdot R_P \cdot C_P$	⇧

[1] *E. Barsoukov, and J. R. Macdonald, Impedance Spectroscopy: Theory, Experiment, and Applications, 2nd Edn., John Wiley & Sons, 2005*
M. Grossi and B. Riccò, J. Sens. Sens. Syst., 6, 303–325, 2017

2 Experimental: the measurement setup and sample description

A schematic representation of the circuit is showed in Figure 1**Fout! Verwijzingsbron niet gevonden.**. This is a plane-parallel configuration of the measurement cell: the electrodes are metallic discs with 10mm radius and the distance between electrodes can be varied. Using a syringe or a small pipet, the liquids can be sampled between the electrodes.

As a measurement strategy we recommend always to measure the empty cell before measuring the sample. If the sample contains water that evaporates at the sample edge, it is good to adjust the sample thickness, so that the full area of the electrodes is covered.

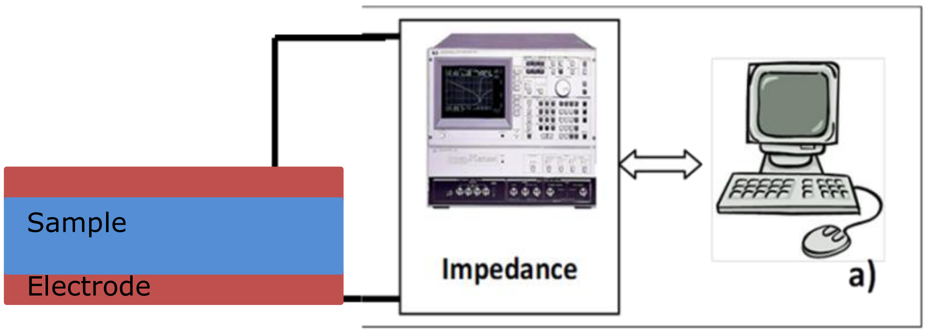

Figure 1*. A sketch of the EIS setup*

Measuring the empty cell for frequency ranged between 1kHz and 10MHz the results show a real capacitive character of the impedance (Figure 2): the argument is -89.64^0 and the modulus is proportional to $(2\pi f)^{-1}$. The corresponding capacity is evaluated at $C_0=1.08\cdot10^{-11}$F

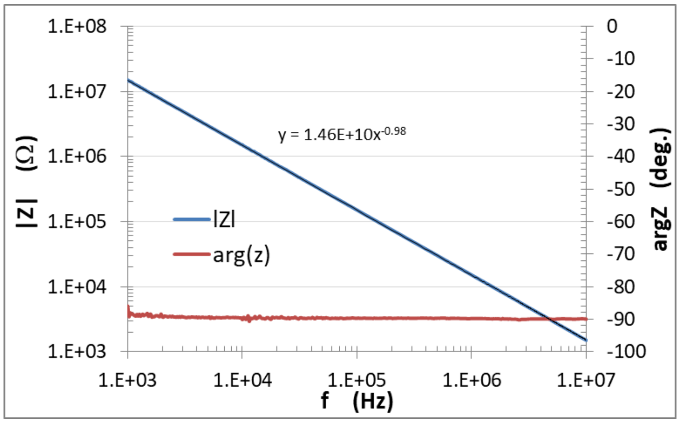

Figure 2. The modulus and the argument for the empty cell measured varying the frequency of the applied voltage from 1kHz to 10MHz

We note that the capacitance of a parallel-plate capacitor is

$$C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot A}{d} \quad (2)$$

where d is the distance between the electrodes A is the surface area of the plate electrodes, ε_0 is the vacuum dielectric permittivity and ε_r is the relative dielectric permittivity of the material. We note that ε_0=8.85·10^{-12} F/m, the relative dielectric constant for air ε_r=1 and the electrode area A=314.15mm^2.

The electrical resistance of material between the electrodes can be expressed as:

$$R = \frac{\rho \cdot d}{A} \quad (3)$$

with ρ – the material resistivity.

3 Experimental results

3.1 Empty cell measurements

Varying the distance between the parallel-plate electrodes the measured data are given in *Figure 3*. Simply we conclude that it is a capacitive reactance (argZ ~-90^0) and the capacity varies as a function of distance d. This is expected and the the plot of C=f(1.d) is shown in *Figure 4*.

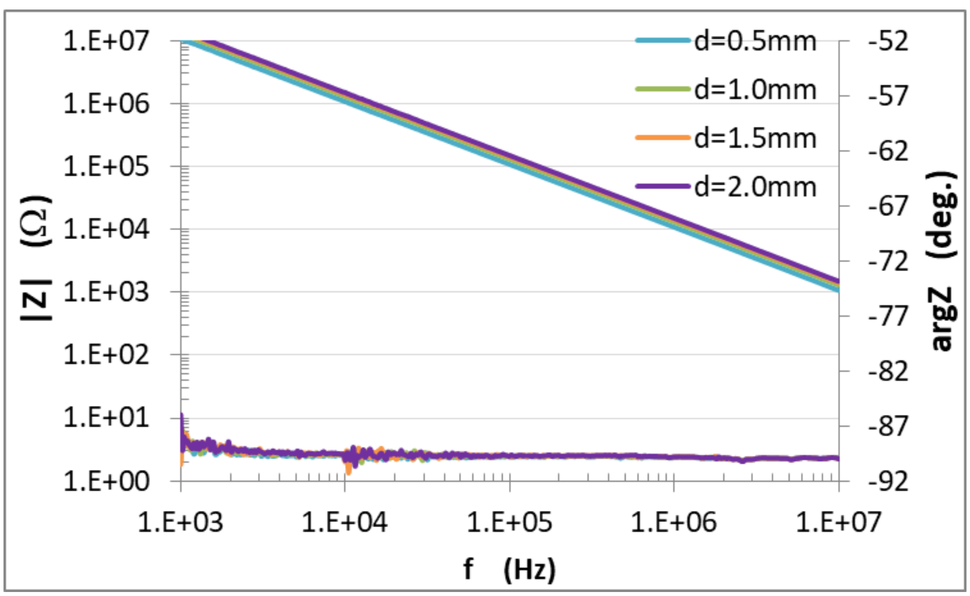

Figure 3. The modulus and the argument of the impedance measured on empty cell, when the distance between electrodes was 0.5, 1, 1.5 and respectively 2 mm.

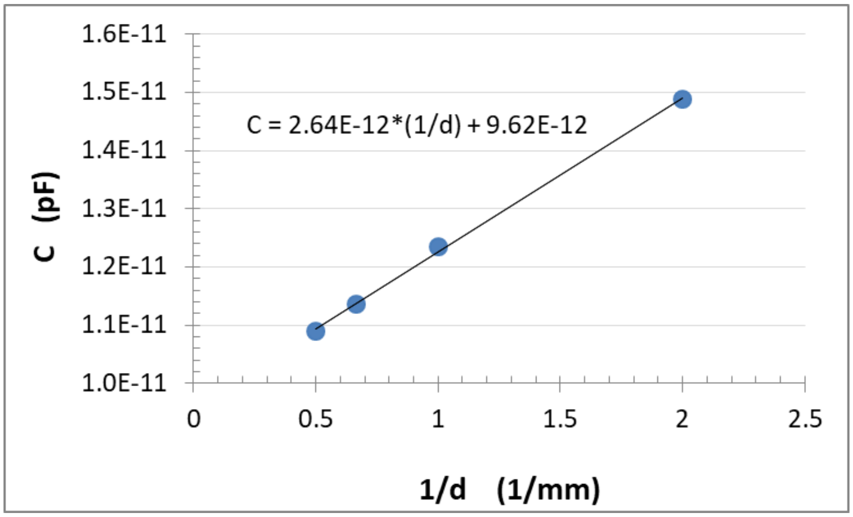

Figure 4. The capacity calculated from the data measurements of Figure 3 and represented as a function of 1/d.

3.2 Measurements on UHQ water

The measurements performed on UHQ water using the same frequency range have been performed.

Firstly we compare the results for d= 0.5mm of the measurements on empty cell and those on UHQ water into the measurement cell. The results are shown in *Figure 5*. At the first seeing, one can say" i) for frequency smaller than $1{\cdot}10^5$ Hz, the UHQ sample shows a resistive character: the argument is almost 0 degree and the modulus is independent on frequency; ii) for f>$2{\cdot}10^6$ Hz the capacitive character become preponderant.

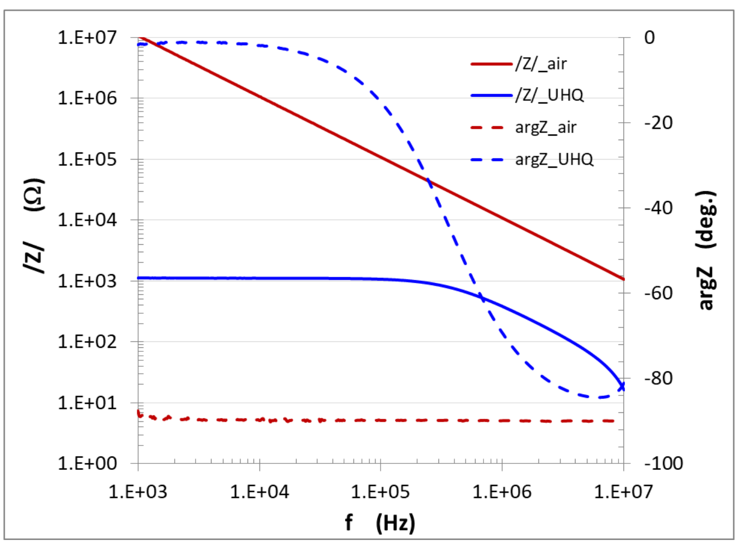

Figure 5. The measured modulus and argument impedance for empty cell (labeled _air) and cell full with UHQ water (labeled _UHQ)

At low frequency the electrical charge from water can follow the applied voltage, while for larger frequency values their mobility dramatically decreases and the sample reveals a capacitive behavior (similar frequency dependency of the modulus as for the empty measurement cell; also, the argZ is -83.5^0).

It is interesting to discuss here about the electrical circuit formed from resistor and capacitor that will produce similar variations. From *Figure 5*, we can say that increasing the frequency, the modulus decreases for f> 2 10^5 Hz, and the argument increases in absolute values. Comparing with *Table 1*, it is clear that the assigned circuit is an R-C parallel circuit. Probably f= 2 10^5 Hz corresponds to $1 \leq \omega^2 R^2 C^2$.

What happens when varying the distance between electrodes?
For the situation when water is between the electrodes, the results are showed in *Figure 6.*

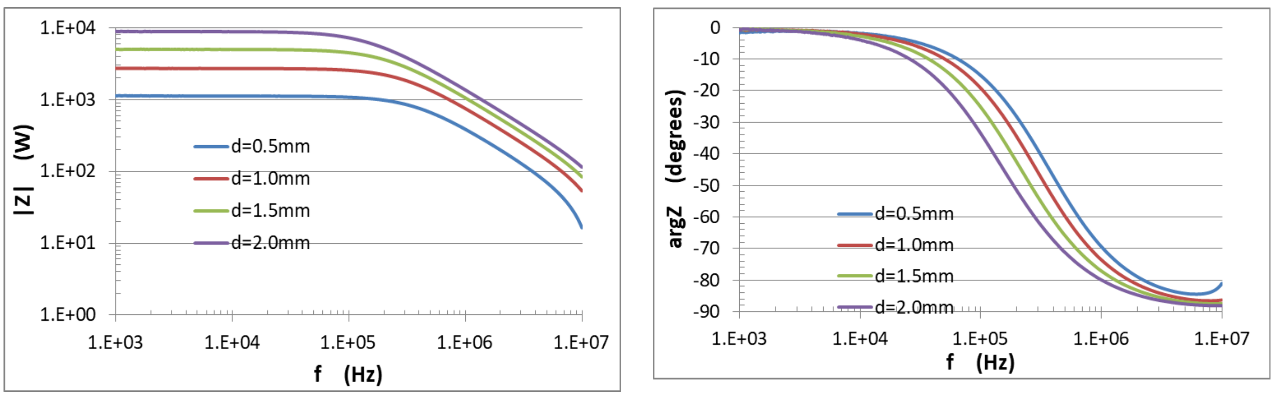

Figure 6. The modulus and the argument of the impedance versus the frequency of the applied potential for UHQ water in the measurement cell when the distance between the parallel-plates was varied

Increasing the thickness on the investigated sample, according to rel. (3), the electrical resistance increases, while the electrical capacity decreases (see rel. (2)). This is equivalent with an increasing in the total impedance, considering the resistor and the capacitor in parallel. And this is showed in Figure 6.

With this idea, the capacity can be calculated from the modulus and the argument for each configuration of the measurement cell and for each frequency value. In *Figure 7* the results of such calculations are shown for frequency f=10^4 Hz. This is interesting because the slope of the trend contains the relative dielectric constant of water.

Indeed, considering the rel. (2), for the case of empty cell and the case of UHQ water in cell, from *Figure 4* and *Figure 7*, we can write:

$$\varepsilon_r^{UHQ} = \frac{\text{slope\_}Figure\ \mathbf{7}}{\text{slope\_}Figure\ \mathbf{4}} = \frac{2.3 \cdot 10^{-10}}{2.6 \cdot 10^{-12}} = 87.12$$

And this is a realistic value.

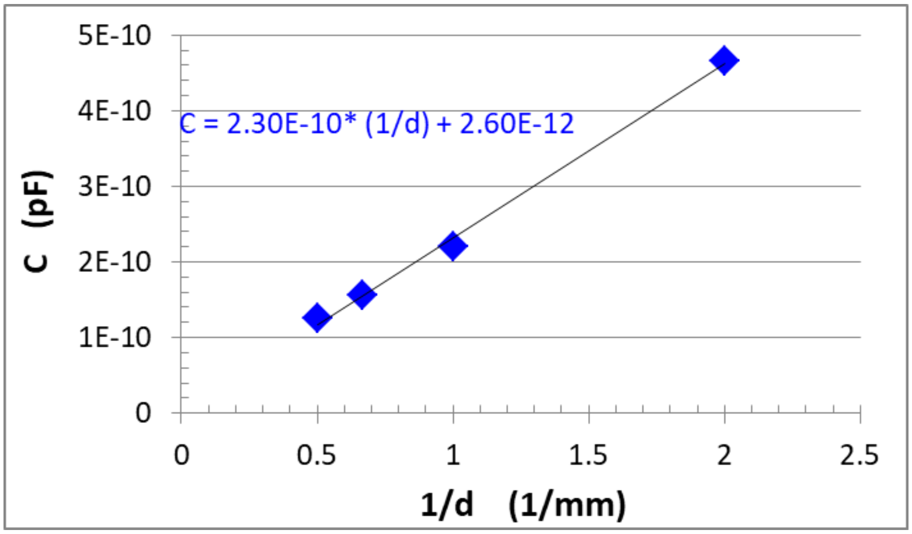

Figure 7. The capacity calculated from the data measurements of Figure 3 and represented as a function of 1/d, for f=10kHz.

4 Conclusion

The EIS measurement setup can be used to determine the dielectric constants for liquid samples, too. It is important to find out the equivalent circuit of discrete elements (resistors, capacitors, inductances) that correspond to the measured samples. Difficulties may appear when the samples characteristics vary in time (e.g. phase transformation) and the equivalent circuit changes.

In this work we show the measurement technique and an example for characterizing the sample of UHQ water. The measurements are made having as reference the empty measurement cell. Having an physical process (e.g. water evaporation, or penetration into a porous material) the EIS can be successfully used to characterize its dynamics[2].

[2] *N. Tomozeiu, Transport in Porous Media · (2016) Vol. 115, No. 3, pp 603-629, https://doi.org/10.1007/s11242-016-0683-1*