

# Application of the Electrical Impedance Spectroscopy in the Electrochemical Cell Constant Determination

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## 1. Introduction

Electrical impedance and its frequency characteristic is one of the most important features of any material regardless to the material phase. That is why the method of electrical impedance spectroscopy (EIS) has become very popular in the last two decades in material science. The idea of the electrochemical sensors application in impedance spectroscopy of liquid conductive materials (electrolytes) requires determination of the resistive cell (sensor) constant and its frequency characteristic. The methodology of the measurement and instrumentation used are described. The results, that have been achieved, are shown and discussed.

### 1.1. Electrical impedance

Electrical impedance describes the measured plant behaviour in electrical field, as its capability to conduct electrical current, or its dielectric or its inductive properties are concerned. To express these physical quantities mathematically, it is necessary to use the complex numbers. In this case, the electrical impedance is usually written as the complex number

$$Z = R + jX$$

R is the real part of the impedance, which is the electrical resistance of the material, j is the imaginary unit and X is the imaginary part of the impedance, which is the reactive (wattles) resistance. If the impedance is placed in the complex plane  $\text{Im} = f(\text{Re})$ , it creates a vector which is turned to the real axis by the angle  $\varphi$ , called phase. In many cases, the impedance is expressed in polar or trigonometric forms:

$$Z = |Z|.e^{-j\varphi} \quad \text{or} \quad Z = |Z|. \cos\varphi + j. |Z|. \sin\varphi$$

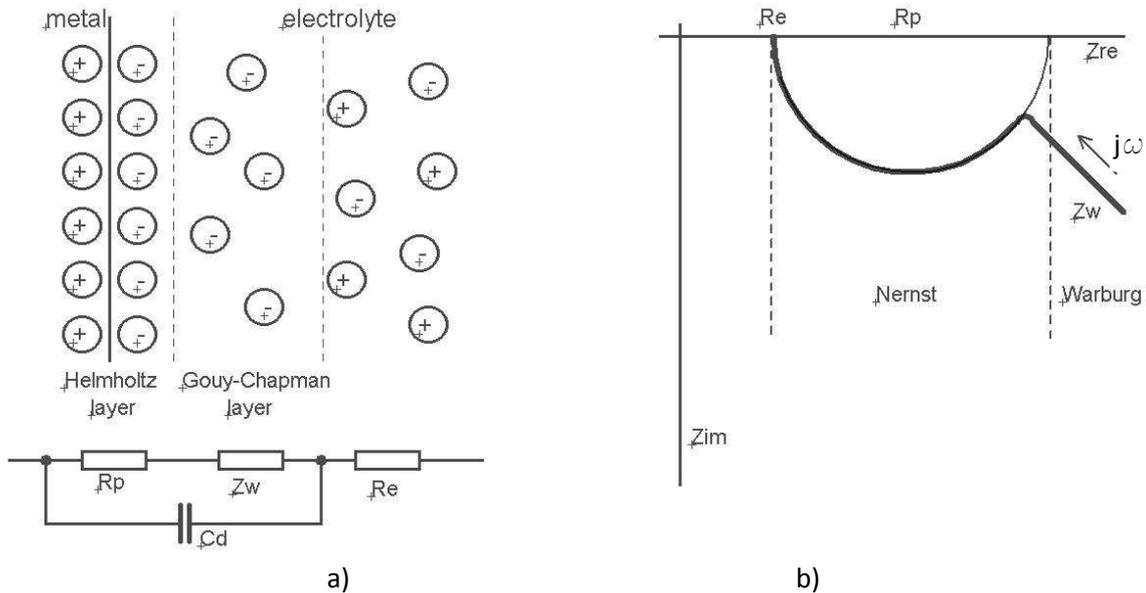
$|Z|$  is the module of the impedance vector, which determines its length, and its given:

$$|Z| = \sqrt{R^2 + X^2}$$

Generally, both, the real and imaginary parts of the impedance change their magnitude with frequency of the supplying AC signal. This is the reason why the spectral measurements of the impedance are worked out.

## 1.2. Electrode effects

Before the measurement is to be done, it would be suitable to describe the phenomena influencing the impedance of the electrode system (electrochemical sensor) placed in an electrolyte. When the metal electrode is put to an electrolyte, the effects shown in Fig. 1 occur [2].



**Fig.1** (a) Helmholtz and Gouy-Chapman layer at metal electrodes in electrolytic solution and (b) Nyquist diagram of the electrode impedance

The atoms at a metal surface in electrolytic contact are ionized. These positively charged ions attract negatively charged ions which create a rigid double layer (Helmholtz-layer). The electrostatic forces vanish with a distance to the metal but they are sufficient to keep a diffuse layer (Gouy-Chapman-layer). Both layers act like a capacitor and because of mostly immobile charge carriers and they have high resistance. The electron transfer at the surface of a metal electrode yields conduction ( $R_p$ ) between metal and the electrolyte. Quantitatively, it is expressed by the Butler-Volmer-equation. The electrolyte far from the electrode is almost a pure resistor ( $R_e$ ). The conduction within the Gouy-Chapman-layer is covered by diffusion. This yields a continuously increasing impedance  $Z_w$  (Warburg impedance) towards low frequency with a constant phase. Therefore, the electrode polarization is most prominent at low frequencies (Fig.1b) but this effect also increases with the conductivity of the electrolyte contacting the electrode.

## 2. Metrological aspects of electrolyte conductivity measurements

Impedance measurements of liquid materials require special approaches to the methodology of measurement. It is caused by the fact that measured electrical impedance of tested material is determined by the electrode system geometry. Thus, to evaluate material resistivity, it is necessary to know so called the cell constant, which given by the electrode system geometry. In this case, the measured impedance of the material can be expressed as [1]:

$$Z = \rho \cdot C,$$

$Z$  is electrical impedance,  $\rho$  material resistivity and  $C$  the cell constant. The cell constant can be determined by the impedance measurement of a standard electrolyte of known volume at defined temperature. As the standard electrolyte, the KCl solution of defined concentration is applied, because

its resistivity is available in the physical tables. Besides,  $K^+$  and  $Cl^-$  ions have almost the same ionic mobility, which reduces diffusion potentials and the conductivity of KCl depends linearly on the concentration up to 2 mol/L. Measuring the impedance in a wide frequency range makes possible to get the cell constant frequency characteristic:

$$C(\omega) = \frac{Z(\omega)}{\rho}$$

This equation shows the proportionality between the cell constant and standard solution impedance frequency characteristics.

### 3. Instrumentation

For the measurement, a new impedance spectrometer ZM-04, produced by HAAL Electro, Ltd. (Czech Rep.) has been used. This instrument has been primarily designed for routine impedance measurements in quality control in food industry plants. That is why it has been designed as the hand – held equipment capable of the automating impedance measurements of conductive biological objects in frequency domain.

Its features are described in following table:

Impedance range:	10 $\Omega$ to 10 k $\Omega$ in sub-ranges of 20, 50, 100 and 500 $\Omega$
Impedance module resolution:	1 $\Omega$
Phase resolution:	1 $^\circ$
Frequency range:	1 kHz to 50 kHz in 1 kHz steps
Electrode system:	2 electrodes
Power supply:	Li-on accumulator KONNOC LIR 123, 3.6 V/ 800 mAhrs
Battery charging:	via USB or AC/DC adapter (accessory)
Charging connector:	5.5/2.1 mm or USB
Measurement and calibration:	automatic in all frequency range, Automatic calibration takes advantage of standard resistors, that are the instrument accessories
Dimensions:	175 x 90 x 25 mm
Weight (inc. accumulator):	185 g
Operating temperature:	-10 - +70 $^\circ C$



Fig. 2. Automatic impedance spectrometer HAAL Elektro ZM-04, that has been used for electrochemical cell impedance characteristic.

As visible, the system is controlled by three pushbuttons which make possible to set the impedance range, elect mode of operation between calibration and measurement and start the experiment in elected mode. All spectrum measurement duration is about 30 s. The results can be transferred to the PC via the USB line. The transferred results are stored there in the form of Excel table and can be further processed.

#### 4. Measurement and results discussion

According to the standard requirements, the KCl solution of defined concentration has been used. The concentrations used were determined by formula:

$$C = \frac{1}{2^n} \text{ mol}$$

The measurement began by the Z-meter calibration using the including standard resistor which represented the real impedance that was measured in all frequency spectrum. Then, the sensor, dived to the standard solution, was connected to the instrument and its impedance spectrum was measured. Between measurements, the sensor was washed by distilled water.

The results achieved are shown in following pictures.

The frequency spectrum of the real part of measured impedances is in the Fig. 3. It is visible that resistance of the electrolyte decreases with its concentration (increases its conductivity). The only exception is the case 1/128 mol concentration (maybe no KCl was added to the solution).

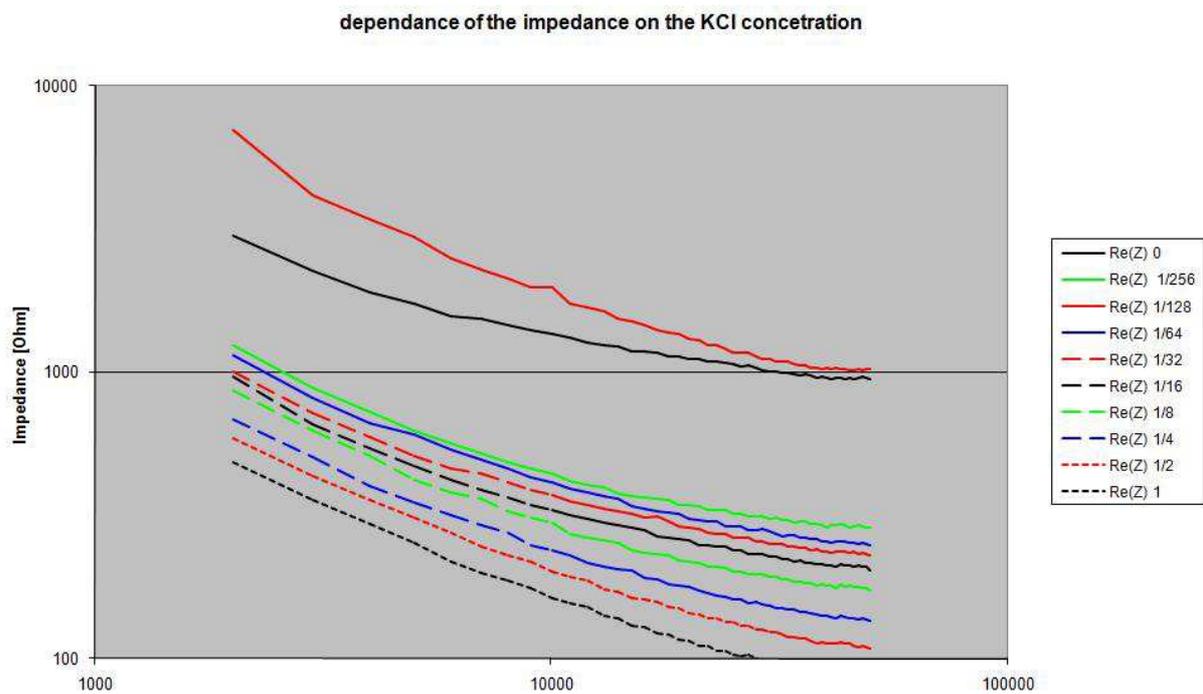


Fig. 3. Frequency spectrum of the measured impedance real part.

The frequency spectrum of the imaginary part is in the Fig. 4. This diagram shows absolute magnitude of this component. Actually, it has negative sign to inform about its capacitive character.

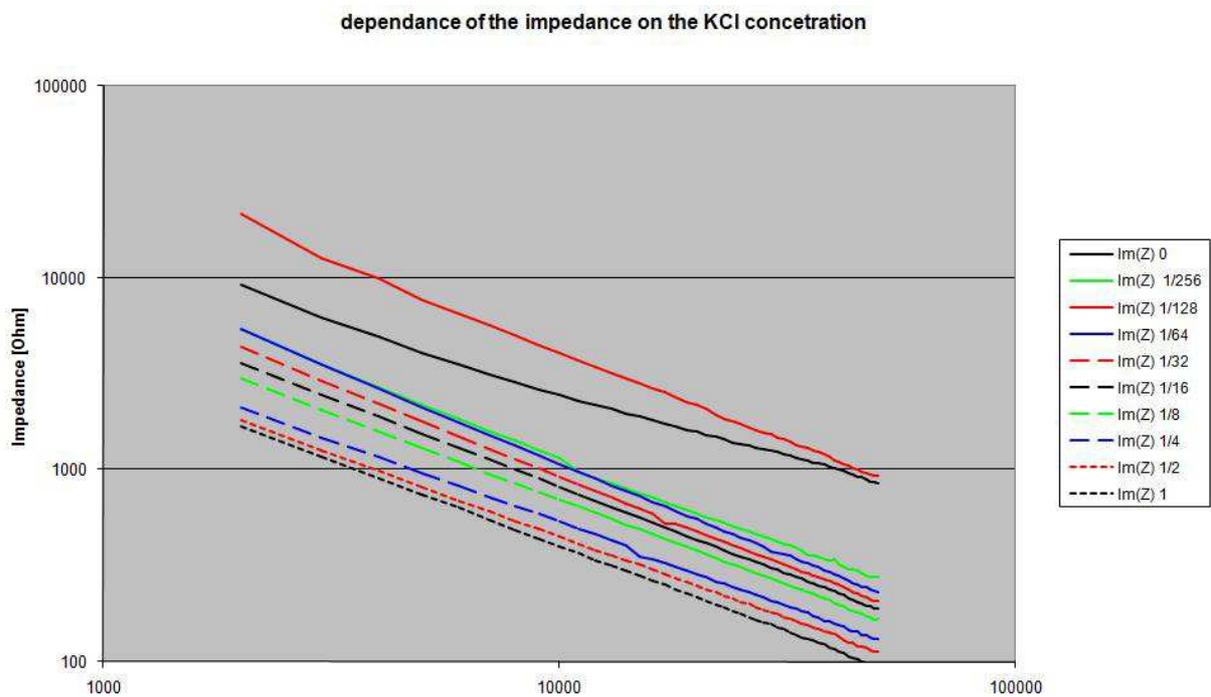


Fig. 4. Frequency spectrum of the measured impedance imaginary part.

Finally, the frequency spectrum of the impedance module is shown in the Fig. 5. Mention the dominating contribution of the imaginary part to the module magnitude.

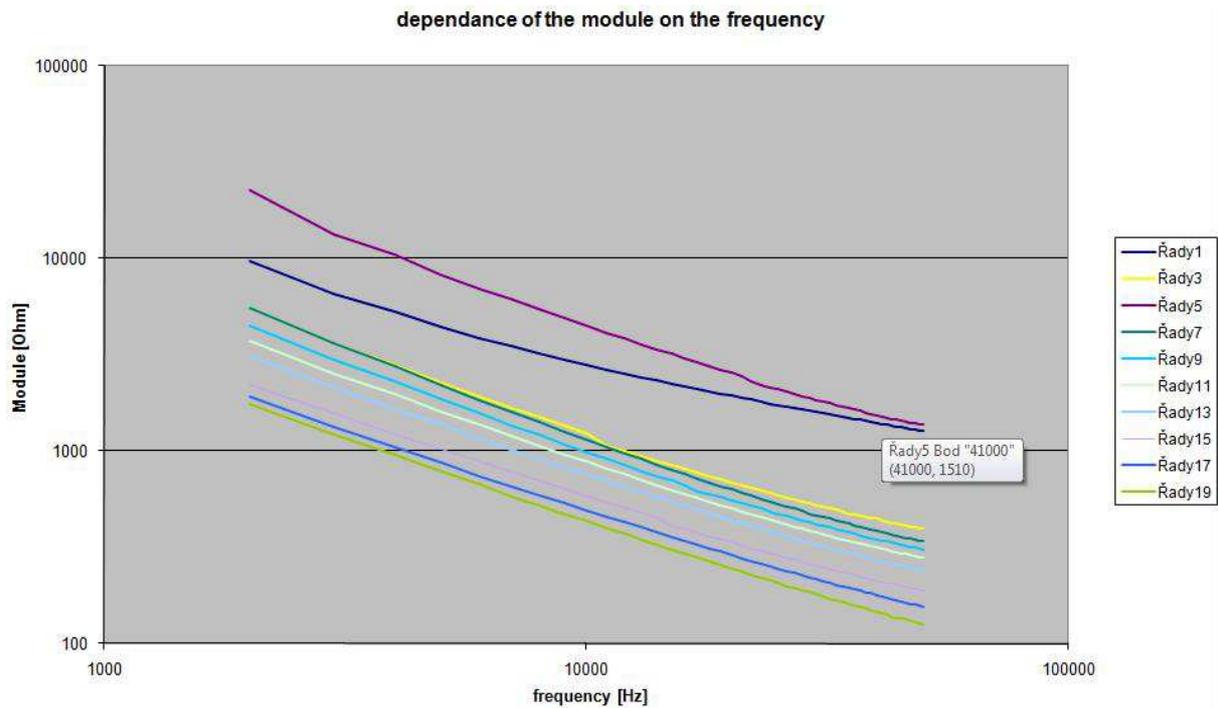


Fig. 5. Frequency spectrum of the measured impedance module.

## 5. Literature

- [1] Krejčí, V., Stupka, J.: Electrical Measurements, p. 254 – 255, SNTL Prague, 1973 (in Czech).
- [2] Pliquet, U.: Bioimpedance: A Review for Food Processing, Food Eng Rev (2010), Springer Science+Business Media, LLC 2010.