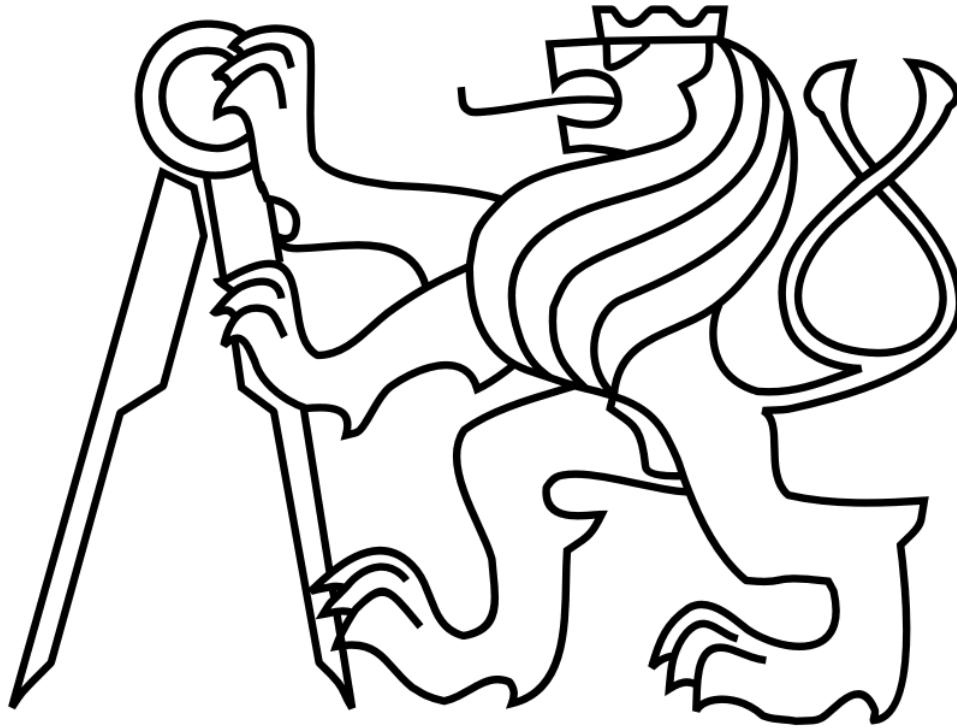


**CZECH TECHNICAL UNIVERSITY IN PRAGUE
FACULTY OF ELECTRICAL ENGINEERING
DEPARTMENT OF PHYSICS**



Bachelor Thesis

**Popis a rozbor matematického modelu impedanční charakteristiky interdigitálních senzorů
pokrytých nanočásticemi**

**Description and Analysis of the Mathematical Model of Impedance Characteristics of
Nanoparticle Covered Interdigitated Sensors**

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Guidelines:

1. Review topics connected to interdigitated sensors, nanoparticles, impedance measurement, impedance spectroscopy.
2. Data analysis with usage of different free softwares.
3. Compare results and discussion.

Bibliography / sources:

- [1] Arnault J. Ch.: Nanodiamonds, Elsevier, Eastbourne, UK, 2017, ISBN 978-0-323-43029-6
[2] McAdams, E.T., A. Lacknermeier, J.A. McLaughlin, D. Macken, and J. Jossinet. "The Linear and Non-Linear Electrical Properties of the Electrode-Electrolyte Interface." Biosensors and Bioelectronics 10, no. 1 (January 1, 1995): 67–74. [https://doi.org/10.1016/0956-5663\(95\)96795-Z](https://doi.org/10.1016/0956-5663(95)96795-Z).
[3] Suni, Ian. Impedance Methods for Electrochemical Sensors Using Nanomaterials. Vol. 27, 2008. <https://doi.org/10.1016/j.trac.2008.03.012>.

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Signature

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Abstract

This Bachelor thesis is dedicated to introduce and review the background knowledge and history of Electrochemical Impedance Spectroscopy (EIS) with its measurement and apparatus, including the background theory of Electrochemistry, Sensors and Nanoparticles. Then, we use the given dataset to test 2 free software on EIS measurement and analysis the obtained result, compare the different mathematical model by analyzing the results from the applied relevant equivalence circuits to this data set. By comparing the different, we will be able to decide the advantages and disadvantages of each software. In the end, we discuss the results and draw a conclusion from it.

This thesis mainly focused on the characteristic of the mathematical model of the EIS. But the analysis of the mathematical model must base on the analysis of the equivalent circuit. So it is not possible to talk about the mathematical model separately, and actually, the objective of the thesis has been transformed to the discussion about the equivalent circuit, the key of the mathematical model and their relationship together with the measurements and the usage of the relevant software.

Keywords

Electric Impedance Spectroscopy; Gold Nanoparticles; Interdigitated sensors; Impedance measurements; Analyte detection; Equivalent Circuit.

Abstraktní

Tato bakalářská práce seznamuje se základními znalostmi a historií elektrochemické impedanční spektroskopie (EIS). V práci je též popsán způsob měření EIS, a dále jsou zmíněny i souvislosti týkající se přesahů do elektrochemie, teorie senzorů a nanočástic. Hlavním těžištěm práce je zpracování dat, v tomto případě ve dvou různých programech, který slouží primárně k nalezení vhodných prokladů různých typů závislostí spojených s metodou EIS. V jednotlivých programech byl vždy hledán optimální náhradní obvod a následně byly vypočteny parametry pro jednotlivé získané závislosti, výsledky byly analyzovány. Na základě porovnání různých možností bylo diskutováno o výhodách a nevýhodách každého softwaru a následně byly vyvozeny závěry.

Tato práce se věnuje především charakteristice matematického modelu ve vztahu k EIS. Analýza matematického modelu musí vždy vycházet především z analýzy náhradního obvodu. Není možné hovořit o matematickém modelu odděleně od náhradního obvodu. Těžištěm práce se stala právě diskuze zaměřená na volbu optimálního náhradního obvodu, který je klíčem k matematickému modelu, a jejich vztahu k výsledkům měření a následnému použití vhodného programu.

Klíčová slova

Elektrická impedanční spektroskopie; Zlaté nanočástice; IDT senzory; Měření impedance; Detekce analytů; Náhradní obvod.

List of Abbreviations

H-DND: Hydrogenated detonation nanodiamond

AuNP: Gold nanoparticles 20 nm diameter, OD 1, stabilized suspension in citrate buffer

1-EN-142/EN drug: Multitarget anti-Alzheimer drug

EC: Equivalent circuit

EIS: Electrochemical impedance spectroscopy

Chsq: Chi-squared test

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Chapter 1: Introduction and Description

1.1 Introduction

Electrochemistry is an interdisciplinary science between, as the name suggests, electrical science and chemistry, it is the study of the interaction between electricity and chemical reactions. The achievements of electrochemical technology are closely related to the reality of human life and production, such as chemical batteries, corrosion protection, surface finishing, metal refining, electrochemical sensors, etc [1].

EIS (Electrochemical Impedance Spectroscopy), which was called as AC impedance in the early scientific papers, was used as a method to study and test the linear circuit in AC analysis; Then, it was applied for the study of the electrode, become a popular experimental method to study Electrochemistry [2].

With further research, in order to increase the sensitivity of the interdigitated sensors during the EIS process, scientists covered it with the nanoparticles to get better results. They found out, the electrode covered by nanoparticles like Au nanoparticles (AuNP) or Carbon nanotube can increase the electrochemistry signals significantly [3]. The reason is the AuNP can increase the electrocatalysis and the carbon nanotubes can increase the surface. So it opened a new door for the EIS study because it can have even better application in the field of biosensor including Antibody-Based sensor, DNA-Based sensor and so on [4].

Based on the brief introduction above, this thesis will explain in detail in an easy and simple way how does EIS play an important role in the Electrochemistry and how its characteristics look like with nanoparticle covered interdigitated sensors by analysis its mathematical model and the discussion of the method and result.

We will use 2 software for processing the data and making further analysis and comparison, so we will have a conclusion about the software also.

1.2 Electrochemistry

Electrochemistry was founded in the late 18th century by an Italian physician and anatomist Luigi Galvani, who established a bridge between chemical reactions and electricity on his essay "Commentary on the Effect of Electricity on Muscular Motion" in 1791 where he proposed a "nerve-electrical substance" on biological life forms. It is marked as the birth of the Electrochemistry [5].

The electrochemical system must contain two electrodes separated by an electrolyte and connected by an external electronic conductor. Ions flow from one electrode to the other through the electrolyte, and a complete circuit is formed by electrons flowing through the external conductor.

An electrode is an electron conductor, refers to a material in which electrons are free to move and thus can be used to sense (or control) the potential of an electron. It can be a metal or other electronic conductors such as carbon, an alloy, an intermetallic compound, a transition metal chalcogenide or a semiconductor. In particular, an electrode is considered to be an electron conductor when an electrochemical reaction occurs or some similar action to an adjacent phase occurs. Electron conductivity generally decreases slightly with increasing temperature and is 10^2 to 10^4 S/cm, where West (S) is the reciprocal of ohms.

A key feature of electrochemistry system is that it contains two electrodes that allow electron transport, the electrons being separated by an electrolyte that allows ions to move but blocks the movement of electrons. In order to reach the other electrode from one electrode, the electrons must pass through an external conductive circuit to do work or absorb work in the process.

However, it looks like a chemical redox reaction, but actually there still some difference. The main difference between these two is that in the electrochemical reaction, the reduction occurs at one electrode and oxidation occurs at the other electrode; in the chemical redox reaction, both reduction and oxidation occur at the same position.

In electrochemical reactions, oxidation and reduction are spatially separated. Therefore, a complete redox reaction is divided into two half-cells. The rate of these reactions can be controlled by the potential difference between the electrodes, for example, using an external power source, which is not available in general chemistry. Finally, electrochemical reactions are always heterogeneous, that is, it always occurs at the interface between the electrolyte and the electrode (and may occur in the third phase, such as gaseous or insulating reactants) [5].

In real life, the electrochemistry and its reactions are also used in electrolysis synthesis, environmental management, artificial organs, biological batteries, electrocardiogram, information transmission and so on. Its development has promoted the progress of world science, social and economic development, and solved the problems of energy, transportation, materials, and environment facing human society.

1.3 Nanoparticles

Nanoparticles are particles between 1 and 100 nanometers (nm) in size with a surrounding interfacial layer. The interfacial layer is an integral part of nanoscale matter, fundamentally affecting all of its properties. The interfacial layer typically consists of ions, inorganic and organic molecules. Organic molecules coating inorganic nanoparticles are known as stabilizers, capping and surface ligands, or passivating agents [7].

Recent research shows that the application of nanomaterials plays an important role in the advancement of nanoscience and nanotechnology. Nanostructured materials have a wealth of physical and chemical properties compared to other small or bulk materials. Nanoparticles have unique intrinsic reactivity due to their increased surface area and are ideal for the synthesis of therapeutic drugs. The interaction between nanomaterials and biological systems depends on the type of surface functional groups of the nanoparticles, particle size, particle shape, and aggregation state, as well as cell type, uptake pathway, and targeting organelles.

Among different types of nanomaterials, metal nanoparticles, especially gold nanoparticles (AuNP), have attracted great interest from researchers in different scientific fields due to their unique properties. Since the beginning of the 20th century, scientists have done a lot of research on the existence of anisotropic gold nanoparticles and found that the structure, optical properties, electronic properties, magnetic properties and catalytic properties of anisotropic gold nanoparticles are different from those of spherical gold nanoparticles. And generally superior to spherical gold nanoparticles.

Besides, the AuNP has these advantages in comparison with other nanoparticles: High X-ray absorption coefficient; Easy to synthesize; Precisely controlled particle physicochemical properties; Strong binding affinity for mercaptans, disulfides and amines; Unique adjustable optical and electronic properties and so on. So, it is widely used in nanoelectronics, optoelectronics, catalysis, and biomedicine.

Here we introduce several kinds of AuNPs:

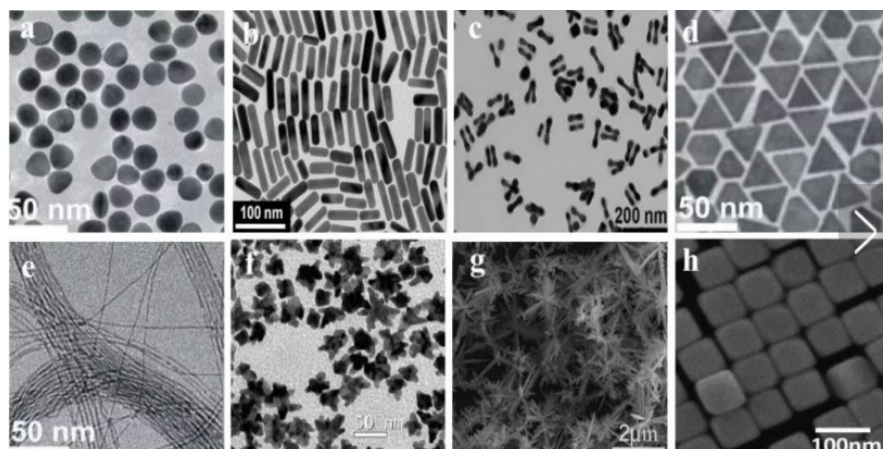


Fig. 1.1 AuNPs in transmission electron microscope (a-f) and in scanning electron microscope(g-h) [8].

As Fig. 1.1 shows, based on the size and dimension of the AuNPs, we can classify them into 4 different AuNPs:

- 1) 0-dimension: Au spherical nanoparticles (a);
- 2) 1-dimension: Au nanorods (b), Au nanolines (e), Au nanotubes, Au nanobelt;
- 3) 2-dimension: Au nanostars (f), Au nanoplates;
- 4) 3-dimension: Au nanoprisms (d), Au nanodumbbells (c), Au nanomultilegs (g), Au nanocubes (h).

Surprisingly, such nanoparticles with small dimensions can have varies kinds, which is incredible. However, in this thesis, we are mostly talking about the Au spherical nanoparticles, it plays an important role in our measurements because one of the most important applications of AuNP is chemical and biological sensing. They have been used as effective sensors for detecting different analytes, such as metal ions, anions, sugars, nucleotides, proteins, and toxins.

According to the sensing strategy, the AuNP sensor has various principles and different types of nanobiosensors utilize different characteristics of AuNP. For example, the basic principle of colorimetric sensors is based on the visible color change caused by the aggregation of gold nanoparticles, the fluorescence sensor utilizes the fluorescence quenching characteristics of AuNP, and the electrical and electrochemical sensors utilize the conductivity of AuNP. High surface area and catalytic properties, AuNP-based surface plasmon resonance sensors utilize the optical properties of AuNP, and bio-barcode determination based on AuNP utilizes the strong binding affinity of gold nanoparticles to thiols and the visible appearance of gold nanoparticles. The color changes to achieve the purpose of detection.

Overall, the AuNP and other Nanoparticles have a very intensive connection with the Electrochemistry measurement, and nowadays researchers are using it quite common.

1.4 Interdigitated Sensors

The sensor is necessary as well as important tools for us to obtain the data from the measurement. Choose a suitable sensor is one of the most important steps at the beginning. In our case, we will introduce the Interdigitated Sensor, which is technically an electrode having a periodic pattern in the shape of a finger or a comb [9]. This type of sensors is widely used in the measurements of Electrochemistry. The sensor operates by reacting with the analyte and producing an electrical signal proportional to the concentration of the analyte.

A typical electrochemical interdigitated sensor consists of a sensing electrode and a counter electrode separated by a thin electrolytic layer. Electrochemical sensors are generally characterized by simple operation and low instrument cost. In addition, electrochemical sensors can be combined with a variety of advanced MEMS (Microelectromechanical systems) manufacturing technologies to enable large-scale mass production and miniaturization to reduce costs.

In this thesis, we will use impedance-based sensors which were fabricated at TESLA Blatná a.s. The model is called Sensor Platform BI2. Its Gold interdigitated electrodes (IDE) are sputtered on the ceramic substrate. The electrode system allows the measurement of various sensitive layers. The structure of the sensitive layer can be applied by various thick- or thin-film technologies. The electrode is interdigitated and the gap between them is 25 μm . The overall size is 5.5 x 8.8 x 0.6 mm^2 . The full parameters and specifications are given in Tab 1.1, and the picture and view of the sensor can be found in Fig 1.2 [10].

| Sensor Platform BI2 | |
|-----------------------------|---|
| IDES: Line/Gap | 25 μm /25 μm |
| Structure of the multilayer | NiCr / Ni / Au |
| Connection | Ag wire \varnothing 0.25 mm |
| Lead Length | 10 \pm 2 mm |
| Temperature range | -30 $^{\circ}\text{C}$ to +200 $^{\circ}\text{C}$ |
| Dimensions | 5.5 x 8.8 x 0.6 mm |

Tab 1.1 Sensor Specifications.

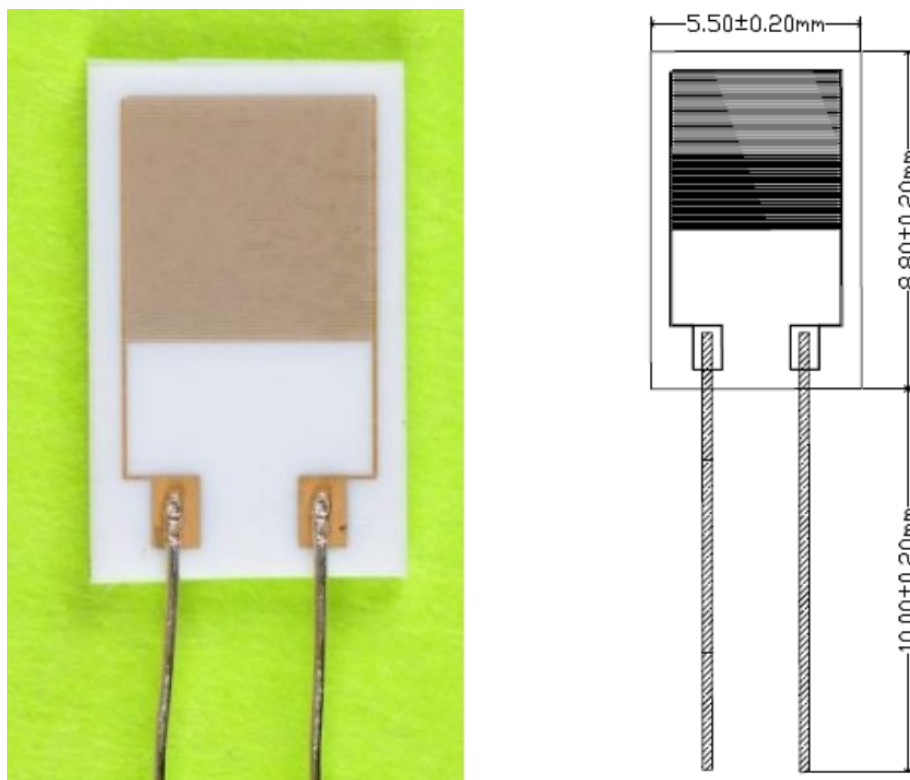


Fig. 1.2 Center view of the interdigitated sensor and its dimensions.

1.5 EIS and its characteristics

Electrochemical impedance spectroscopy (EIS) is now well established as a powerful tool for investigating the mechanisms of electrochemical reactions and is a relatively new technology used in the field of Electrochemistry measurement for measuring the dielectric and transport properties of materials, for exploring the properties of porous electrodes, and for investigating passive surfaces. Although it does not have a long history, it has developed very fast and got widely used also in other fields like in the battery, fuel cells, corrosion, and protection...etc.

Since the EIS is based on the electrochemical reactions, in order to understand the mechanisms of the EIS and its characteristics better, firstly we can use the analogy method to compare the Electrochemistry reaction and an Electric circuit. The most common thing between the electrochemistry reaction and the electric circuit is, if we establish a voltage signal, it will generate a current signal. Because of this connection of “Input-output”, we can link these 2 concepts together.

We know that in a DC circuit, Resistivity is a measure of the material's ability to oppose electric current. If we introduce this concept to an AC circuit, we can get the Impedance (Z), which is the obstruction that AC current encounter. So, we have the Ohm's law for AC:

$$\hat{E} = \hat{I} \cdot Z \quad (1)$$

Where \hat{E} as Voltage, \hat{I} as Current and Z as Impedance.

Because the AC current has the frequency, thus the Impedance will change due to the change of the frequency. In some particular frequency, the impedance will look more close to an electric apparatus, like a resistor or a capacitor.

Based on the evidence above, we can get the kernel knowledge of the Electric Impedance Spectrum (EIS): The whole electrochemistry reaction can be expressed as an Impedance.

During the EIS test procedure, the input signal usually is a sinusoidal AC signal with a small amplitude. With that, we could measure the total impedance of the system, and analyze the equivalence circuit. There are 3 characteristics of the input and output signal: Amplitude, Frequency, and Phase.

The impedance $Z(\omega)$ is a complex number which consists of 2 parts: the real part and the imaginary part. So it can be expressed as:

$$Z(\omega) = Z_{(Re)} - jZ_{(Im)} \quad (2)$$

Where Z_{Re} is the real part and jZ_{Im} is the imaginary part.

Thus, the EIS graph we will obtain are also use these 2 parts as x-axis and y-axis. Here we present 2 simple examples, the red line stands for the EIS spectrum in the figure :

- 1) If there is only one capacitor C exists in the circuit, the EIS spectrum would be a straight line overlapping the y-axis, because there is only the impedance Z with its imaginary part, as Fig. 1.3 shows:

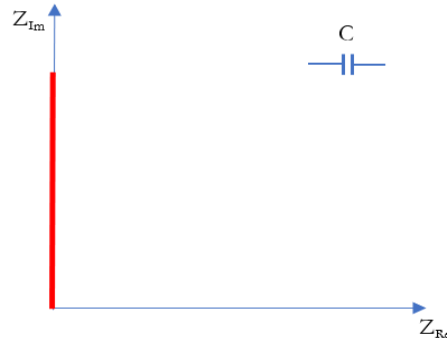


Fig. 1.3 While only the capacitor exist in the circuit.

- 2) While the resistor R connected with capacitor C , we will obtain the real value in the real part of the impedance, which is a straight line perpendicular to the x-axis (Z_{Re}), intersects at point R , as Fig. 1.4 presents:

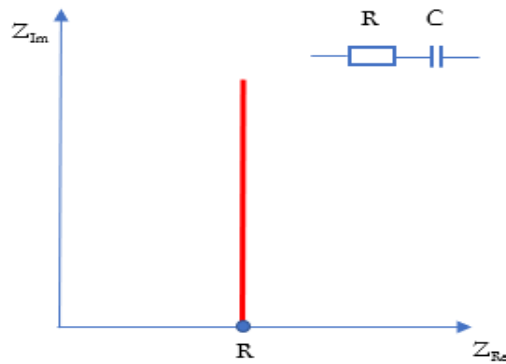


Fig. 1.4 While a resistor and a capacitor connected in series in the circuit.

However, as we can learn from most of the scientific paper about the EIS, the graph look like the following picture: [11]

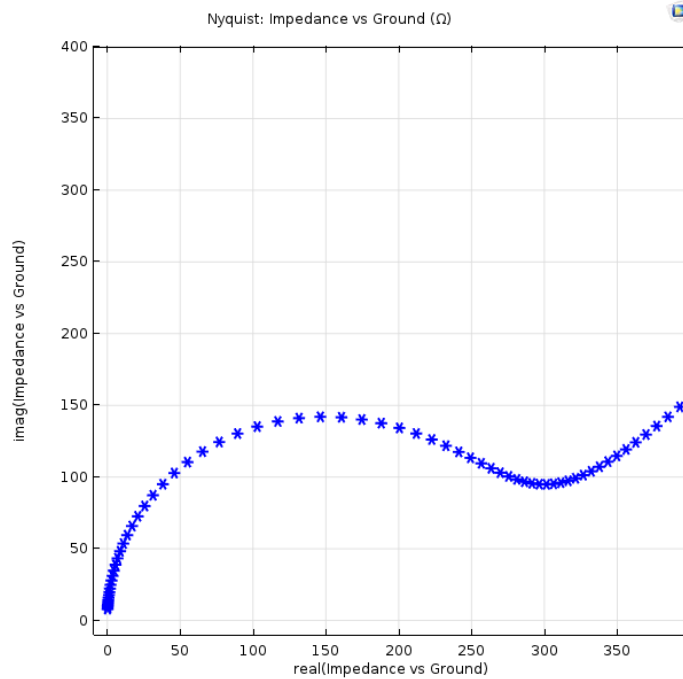


Fig. 1.5 Simulated Nyquist plot from an EIS experiment. Points toward the top right are at lower frequencies (MHz), while those toward the bottom left are at higher frequencies (>100 Hz) [11].

This graph can be approximated as a semi-circle connect with a line segment. Why does it look like that? Here we can explain with the basic model of the typical electrochemistry reaction.

A typical electrochemistry reaction process consists of many elements, including the Electrical Double-Layer Capacitor (EDLC), internal resistance and the Faraday process. Here we draw a graphical explanation to make the process easier to be understood, as Fig. 1.6 shows:

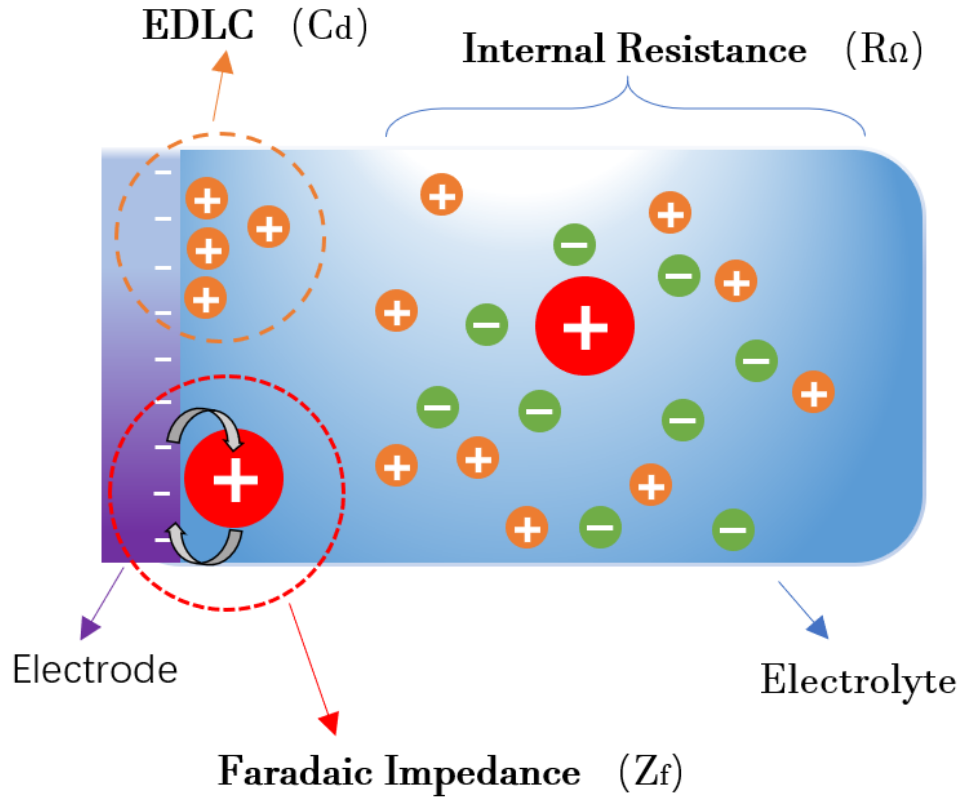


Fig. 1.6 A model of a typical electrochemistry reaction process.

We can abstract 3 electrical components from the above:

1. The EDLC (C_D), comes from the nonactive ions from the Electrolyte, there is no chemical reaction happened, only changes the distribution of the Electric charge.
2. The Faradaic Impedance (Z_f), comes from the active ions from the Electrolyte there is a chemical reaction happened (Reduction-oxidation reaction) which also called Faradaic process.
3. The Internal Resistance (R_Ω), directly from the Electrode and Electrolyte.

Thus, we can obtain the EC as the following Fig. 1.7 presents:

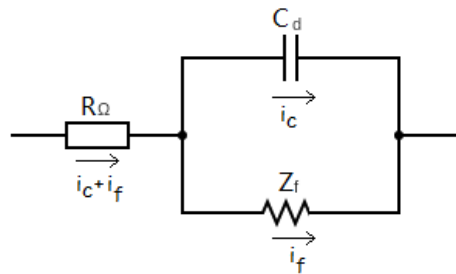


Fig. 1.7 An abstract EC (Randle's EC) including C_d , Z_f , and R_Ω .

This circuit is called Randle's EC, which we will discuss more in Chapter 2. About the Faradaic Impedance (Z_f), it can be divided further into 2 processes: Charge Transfer and Mass Transfer.

These 2 processes can be abstracted into the Resistance of the charge transfer (R_{ct}) and the Warburg Impedance (Z_w) as in Fig. 1.8 shows:

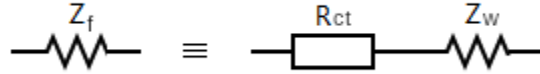


Fig. 1.8 A division of Warburg Impedance (Z_f) to Resistance of the charge transfer (R_{ct}) and Warburg Impedance (Z_w).

According to Fig. 1.8, the real part of the impedance can be expressed as the following mathematical model:

$$Z_{Re} = R_{\Omega} + \frac{R_{ct} + \sigma\omega^{-\frac{1}{2}}}{\left(C_d\sigma\omega^{-\frac{1}{2}} + 1\right)^2 + \omega^2 C_d^2 \left(R_{ct} + \sigma\omega^{-\frac{1}{2}}\right)^2} \quad (3)$$

Meanwhile, the imaginary part can be expressed as:

$$Z_{Im} = \frac{\omega C_d \left(R_{ct} + \sigma\omega^{-\frac{1}{2}}\right)^2 + \sigma\omega^{-\frac{1}{2}} \left(\omega^{-\frac{1}{2}} C_d \sigma + 1\right)}{\left(C_d\sigma\omega^{-\frac{1}{2}} + 1\right)^2 + \omega^2 C_d^2 \left(R_{ct} + \sigma\omega^{-\frac{1}{2}}\right)^2} \quad (4)$$

Where σ is a coefficient of the mass transfer process. Since the formula (3) and (4) is quite complex, we will consider only 2 extreme cases.

1) While ω approaches to 0 (low frequency), the relation between Z_{Re} and Z_{Im} can be simplified as:

$$Z_{Im} = Z_{Re} - R_{\Omega} - R_{ct} + 2\sigma^2 C_d \quad (5)$$

If we plot it, it will be a line with slope k equals to 1, and it will intersect with the x-axis at Z_{Re} , as following Fig. 1.9 shows:

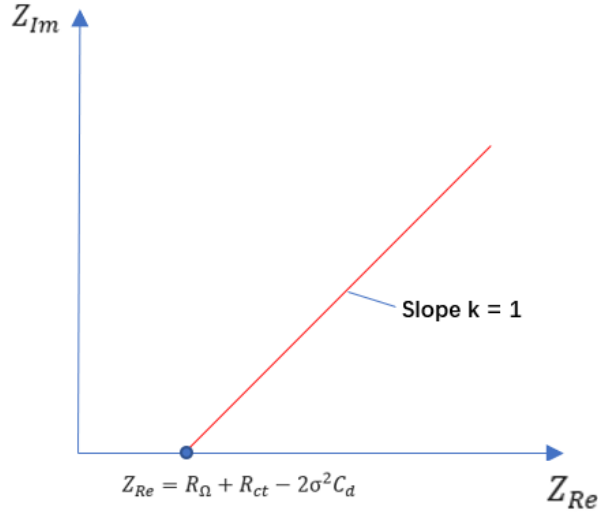


Fig. 1.9 While ω approaches to 0, the graph is a line with slope k is 1.

2) While ω approaches to a large number, at the moment, frequency is very high, the period is very short, so the mass transfer does not happen yet, which means the influence of the Warburg Impedance (Z_w) has disappeared. The EC can be simplified as Fig 1.10 shows:

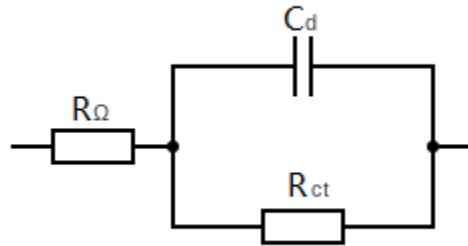


Fig. 1.10 While ω approaches to a large number, the Z_w can be ignored.

For this model, the relation is:

$$\left(Z_{Re} - R_{\Omega} - \frac{R_{ct}}{2} \right)^2 + Z_{Im}^2 = \left(\frac{R_{ct}}{2} \right)^2 \quad (6)$$

With this formula, we can draw the graph, and obtain the following semicircle with the center at $R_{\Omega} + \frac{R_{ct}}{2}$ and the radius is $\frac{R_{ct}}{2}$, presented in Fig. 1.11.

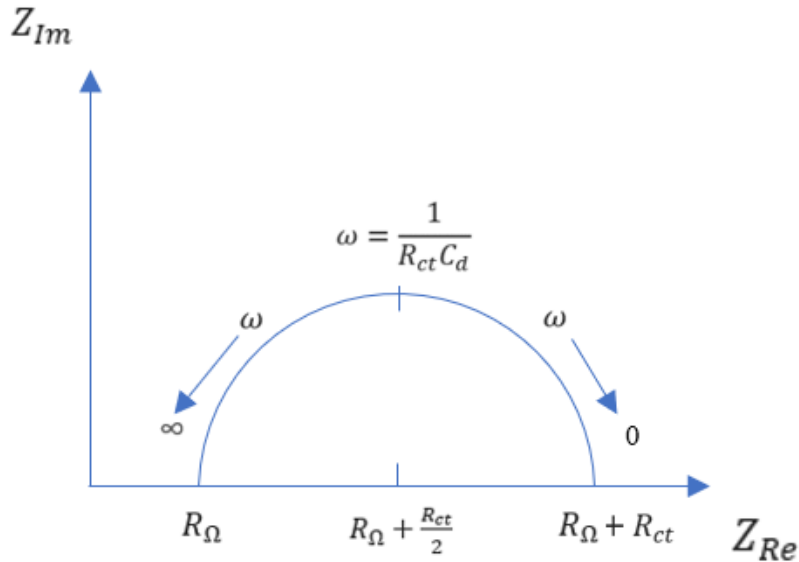


Fig. 1.11 A semicircle obtained while ω approaches to infinity [12].

So, Based on the trend of 1) and 2), we can do the basic analysis of an EIS graph:

The low-frequency part is controlled by Mass-transfer, meanwhile, the high-frequency part is controlled by the Charger-transfer, as following Fig. 1.12 shows:

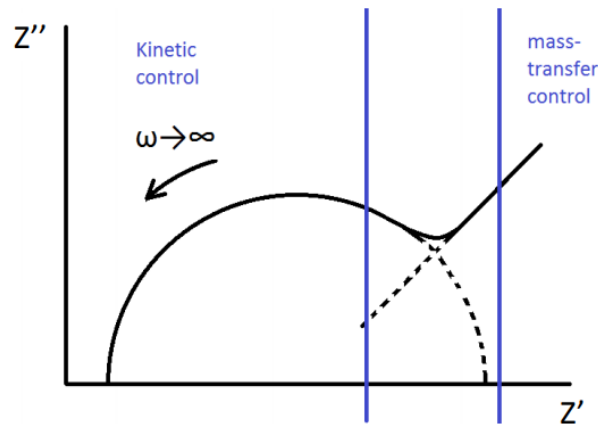


Fig. 1.12 Nyquist plot of the Randles Model showing a semi-circle at high frequencies and a unity slope line at low frequencies [13].

After the above description, we have learned the mechanism behind the EIS and its characteristic, the next step would be to choose an EC according to the measurement and how to do the approximation with it. We will have a further discussion in the next chapter, with several examples running under the relevant software and programs.

Chapter 2: Analysis of the EIS Characteristics by Free Software

2.1 Introduction

In order to understand the EIS and its characteristics better, here we present an example: We will use 2 software to test the given EIS data, find the suitable Equivalent Circuit and make the approximation. We will choose the popular software in the field of EIS analysis, one is called ZSimpwin, the other one is called EIS Spectrum Analyser. Finally, we will compare the result we obtained by another result obtained from other software.

2.2 Description of the Measurement

The measurement is a part of a project which dedicated to finding a cheap way to detect different kind of drugs about their existence and concentrations, which was done by the Department of Physics, Faculty of Electrical Engineering, Czech Technical University. During the measurement, they were using the EIS method for analyzing, so we can use the data to test our software later.

There are 8 sensors in a total of this measurement, with 4 different coated samples:

- 1)The Empty sensor
- 2)The H-DND (Hydrogenated detonation nanodiamonds)
- 3)The H-DND plus AuNP
- 4)The H-DND plus AuNP, together with the 1-EN-142 drugs

And each sensor went through those 4 different coated samples (the substance to be tested), and there are 8 times of measurement, the procedure is exactly the same, but the only difference is the concentration of the 1-En-142 drugs are different in each measurement, so we can also learn how does the concentration of the drugs influence the result. So we have in total of 32 data as the test results.

The model of the device we used for this EIS experiment to measure the impedance is Hioki LCR Meter IM3536, with test fixture Hioki 9261-10.

We do not repeat in details about how to do the complete measurements [15], just briefly introduced the procedure:

First, we clean the sensor, then do the measurement of the empty sensor; Between each measurement, we clean the sensor with pure water. After that, we add the HDND, cover it with the AuNP and EN drugs one after another;

The working mechanism of the device is as we described above in Chapter 1.5, is to input a low-amplitude AC signal, by measuring the ratio of the AC voltage and the AC signal with the change of the frequency. More precisely, we measure the impedance of the sensor with the substance to be tested at variable frequencies starting from low frequency to the highest frequency required. The frequency range is from 42 to 8,000,000 Hz. Since we are measuring very small signal impedance, we will need to make sure the AC voltage should be much smaller than the DC voltage; The AC current should be much smaller than the AC current.

During the measurement, for each frequency, we measure and calculate the impedance in the real part Z_{Re} and the imaginary part Z_{Im} ; In total, we measure 100 times so that we will obtain the result with these 3 types of data: 100 different frequency with the relative impedance (Z_{Re} and Z_{Im}) respectively in each sensor and each measurement.

Once we plot the result, the graph looks like as we calculated before, a semicircle connected with a “tail” (line segment), as the following Fig. 2.1 shows:

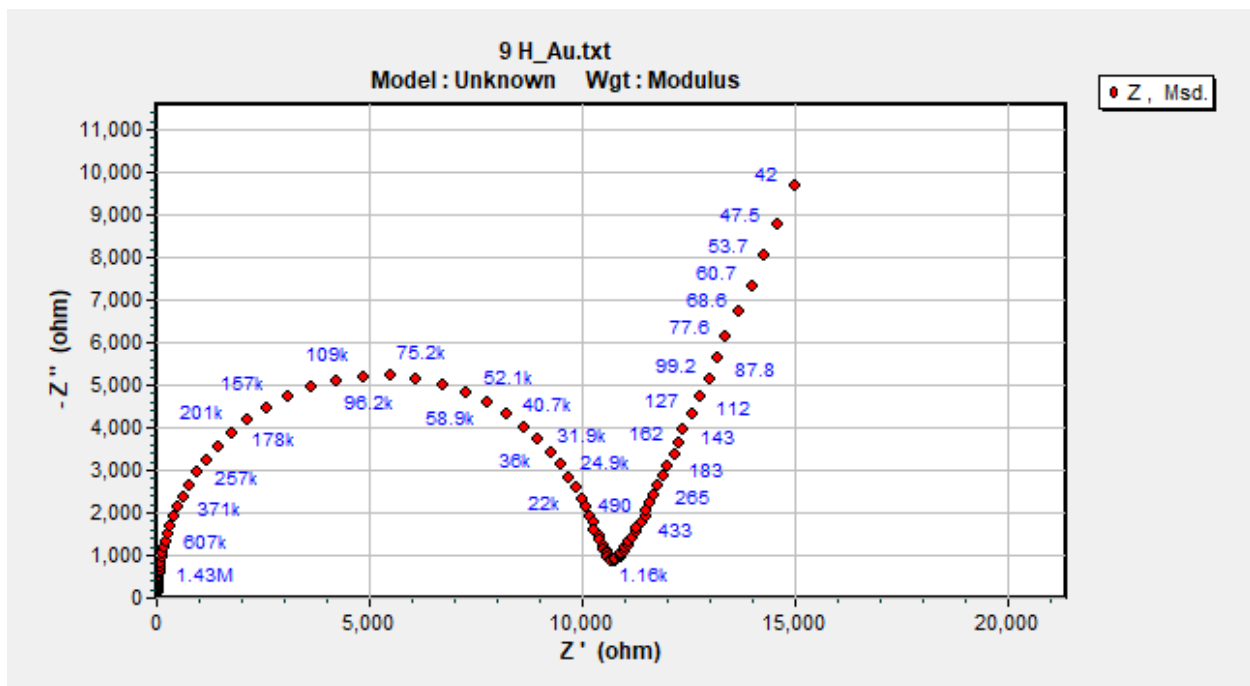


Fig. 2.1 An example of our measured data in the Nyquist plot.

From the figure, we can see as we described also in Chapter 1.5 above, with X-axis as the Real part of the impedance and Y-axis as the Imaginary part of the impedance. The blue number indicates the frequencies, so for each measurement (points in the figure) we can learn its frequency, and its Z_{Re} and Z_{Im} .

Here, we finished the description of the measurement and the data, now we will use our software to analyze it.

2.3 Analysis via software ZSimpWin Demo 3.30d

In order to proceed with the data we obtained on chapter 2.2, here we will use free software, we will test the data on them and try to figure out which one is better and if there is something needed to be improved.

The first software is called ZSimpWin, and we will use the demo version 3.30d. ZSimpWin is an EIS Data Analysis Software integrated with the Versa Studio software to provide straightforward and versatile equivalent circuit model fitting [16].

There are few differences between the demo version and the full version like we cannot copy & paste the result and some external functions are disabled. However, since we are only interested in the EIS part and we can store the result manually, it does not influence our experiment and analysis.

Generally, it looks like this, as Fig. 2.2 shows:

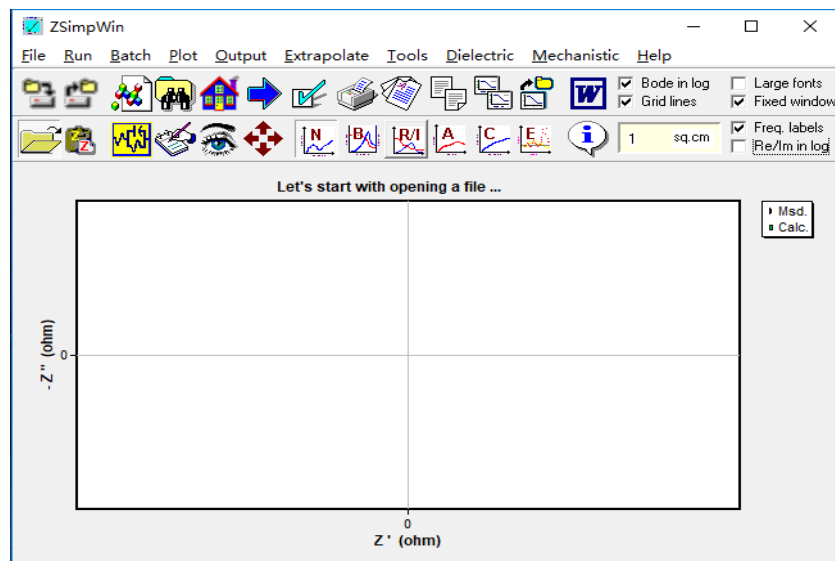


Fig. 2.2 Homepage of ZSimpWinDemo 3.30d.

The central coordinate system is as we described before, here it uses the Z' to represent real part and Z'' for the imaginary part.

Now it's time to process the data. Since we were using 4 different substances (Empty, H-DND, AuNP, and EN drugs) and 8 sensors, we have 32 samples of data to be calculated.

First, we load the data of the first measurement. It is empty sensor No.1, here the file named "01 Empty.txt". It is named as "Empty" because we did not put any substance on the sensor, so we only measure the empty sensor's impedance. After loaded, we can see the input data as we expected in the following figure:

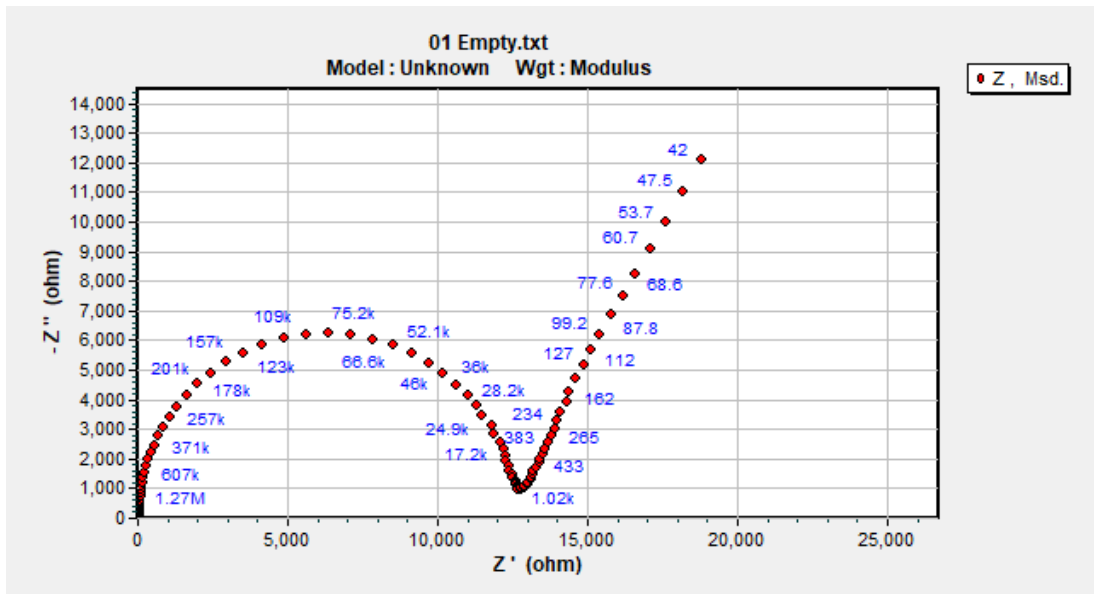


Fig. 2.3 The display of the result of the first measurement.

After that, the next step is to fit this curve by using the appropriate EC.

Here we should point out, that after reading many relevant scientific papers, there does not exist such a so-called "Definitive Conclusion" about how to choose the EC properly. All the other scientists always declare, "According to our measurement, we will choose this EC to get the best result." However, they did not explain why.

So we assume the method to choose the best EC is still a black box for us, and perhaps, there even does not exist such a perfect algorithm or a method to choose the EC, as well as there does not exist one EC can be suitable for all the measurements.

Thus, in this thesis, we will use the so-called “Naive Approach” to obtain the most suitable EC, which is, to test almost all the possibilities, although it is a bit time-consuming.

Luckily, this software has a list of EC to be used, so we will start from the simplest EC combined with simple apparatuses, gradually adds more apparatuses to be more complex, for different purposes to use in a different experiment. Thus firstly, we will choose the Randle’s EC.

We have not introduced Randle’s EC very deeply in the previous chapter, now is the chance. The Randle’s EC is one of the simplest model describing processes at the electrochemical interface. In real electrochemical systems, impedance spectra are usually more complicated and, thus, it may not give appropriate results. We can have a look again about what does the Randle’s EC looks like in Fig. 2.4:

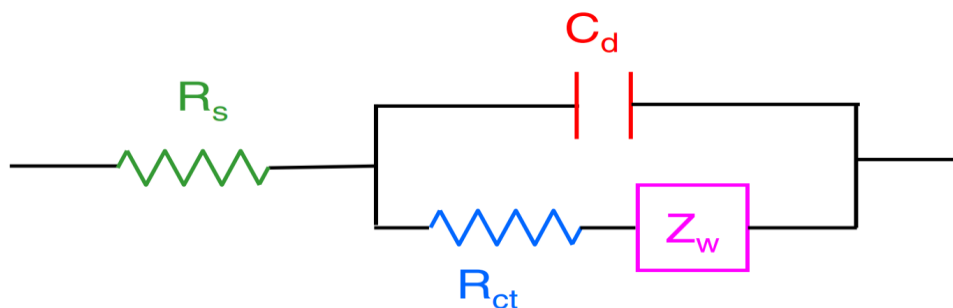


Fig. 2.4 The display of Randle’s EC.

So we will use this for our first try. It can be easily found inside this software under the “Select model and run mode” session, as Fig. 2.5 shows:

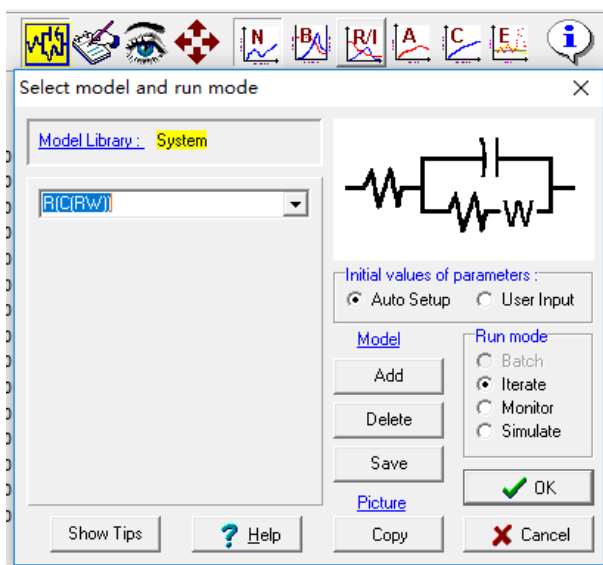


Fig. 2.5 Select model and run mode.

The resistors in this software here are using the symbol of ANSI, so this software is clearly from the US. And then we just click the “ok” to apply this EC on this data., to see the result shown in Fig. 2.6:

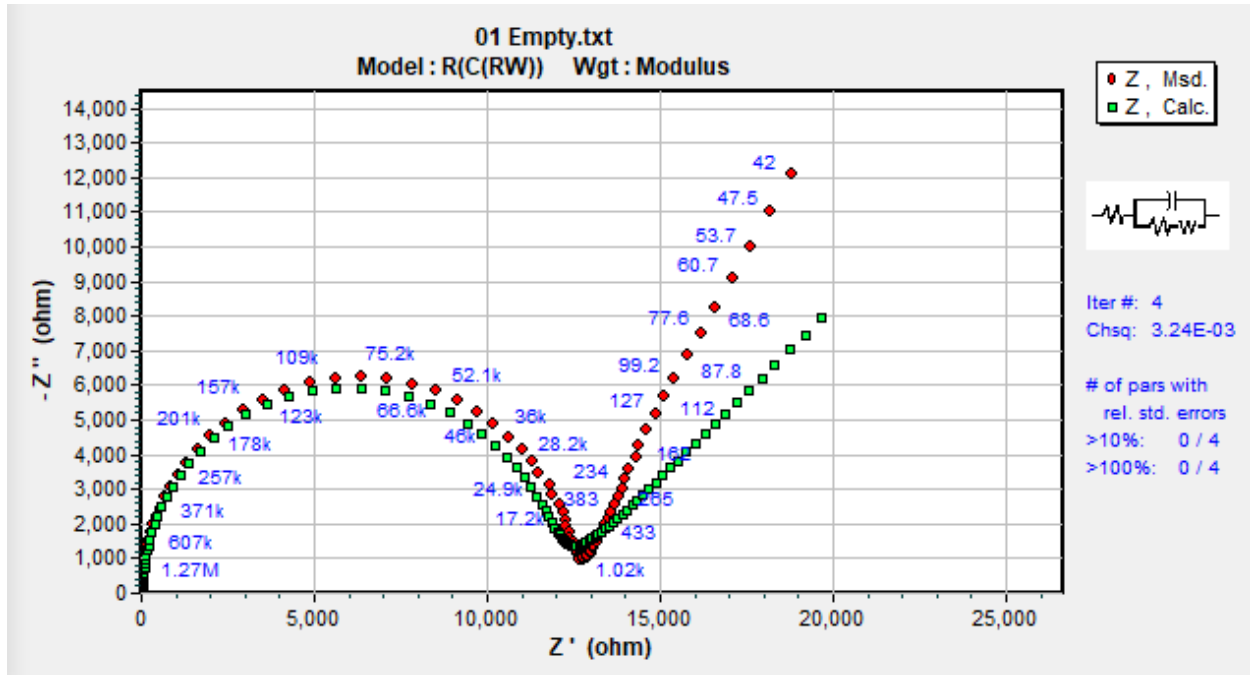


Fig. 2.6 Randle’s EC applied to the first data.

From this figure, we can see that this Randle’s EC works, although it is not that perfect. The red point was the original, meanwhile, the green points are fitted. Obviously, the trend of the fitting is correct, but the precision is not flattering.

According to its documentation, this software is using the Least Square algorithm to do the fitting [16], on the right side we can see that it has been iterated 4 times. (States as Iter #: 4)

Moreover, the most important thing is to check the accuracy, we first use the given Chi-Square distribution states on the right side of this figure, here it notes as “Chsq”. It describes the difference between the original curve and our fitted curve. Here the Chsq is 3.24E-03, the larger of this number, the larger of the difference. 3.24E-03 is kind of large, but acceptable for our first try. Later we will use another calculation to confirm the accuracy.

With the same idea, we will apply this Randle’s EC to the rest of the data. We will omit the result here and discuss it in Chapter 4.

So our first try has finished. However, in order to improve our result, here we will choose a different EC, then we will apply it to the same data, as the following figure shows:

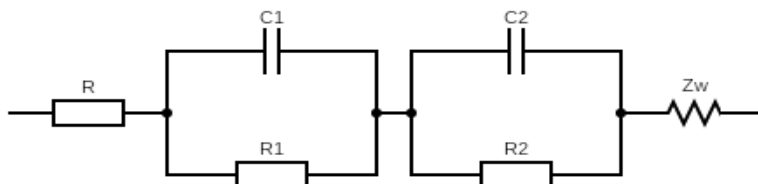


Fig. 2.7 The 2nd EC, consist of 3 resistors, 2 capacitors, and 1 Warburg impedance.

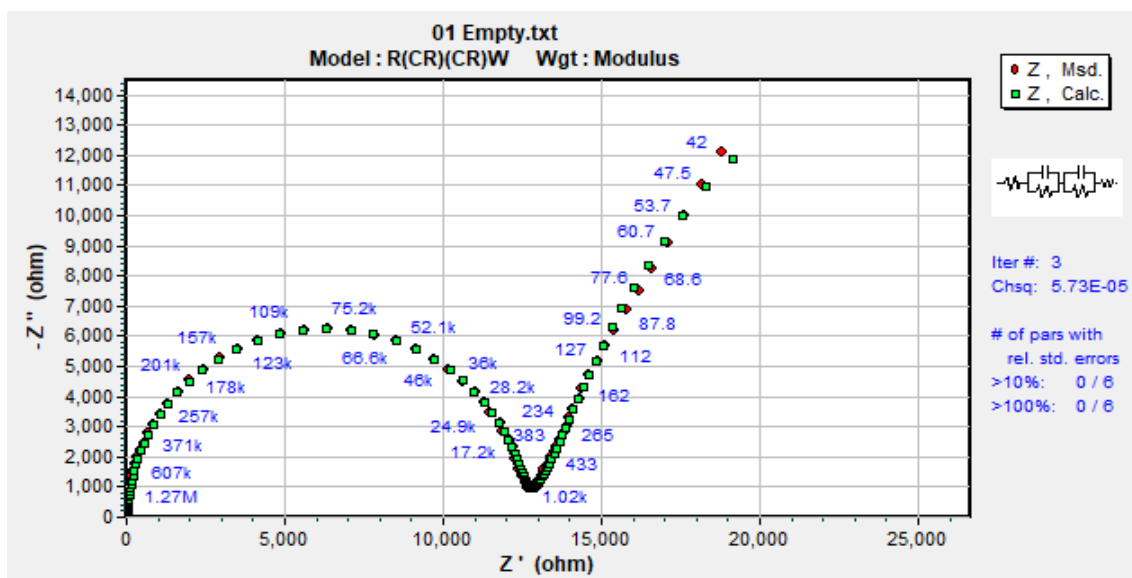


Fig. 2.8 The 2nd EC applied on the 01 Empty.

This time the fitting looks much better. This new EC has one more capacitor and one more resistor compare with the Randle's EC, and there are 3 times of iteration with the Chsq of 5.73E-05, which is 100 times more precise than the Randle's EC.

With this EC, we can apply it on the other 3 types of measurements: the H-DND, the AuNP, and the EN drugs, and we have the result as the following Fig. 2.9 shows:

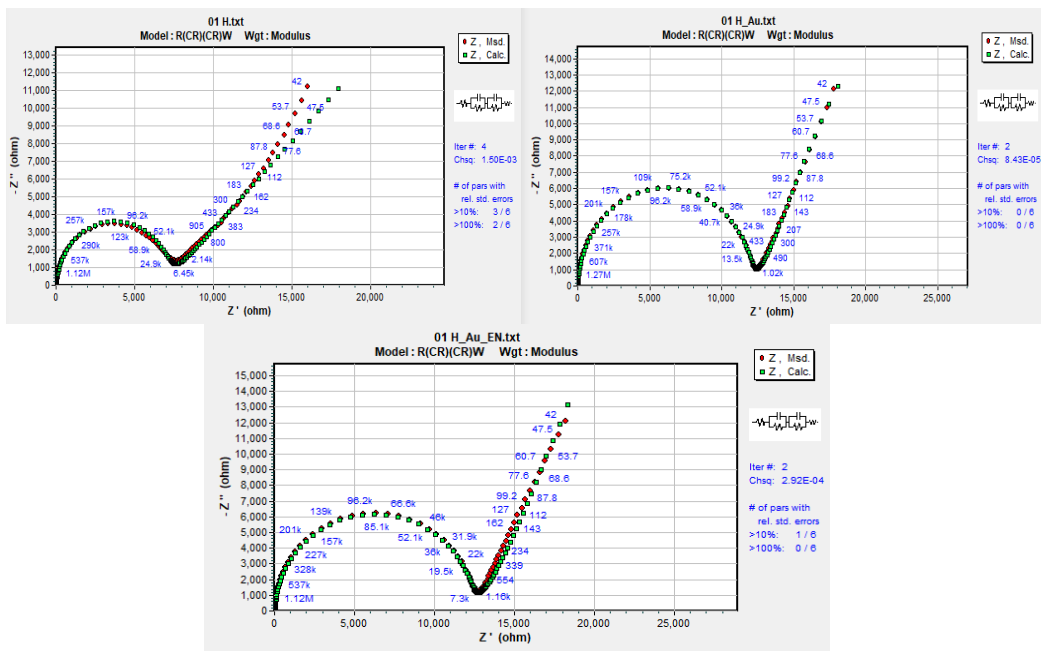


Fig. 2.9 The 2nd EC applied on the H-DND (top-left), with H-DND+AuNP (top-right) and with the H-DND+AuNP+EN drugs (bottom).

As we can read from The average Chsq of these 4 measurements is 4.83E-4, which is still better than the one with Randle’s EC whose average Chsq is 5.73E-3.

Just by using a different EC, we have improved our result by almost 10 times better, so we can learn from it, that choosing a suitable EC is very important and critical. We will go through the rest of the data with this EC and discuss our result later.

Then, we can improve our result even better, by adding more apparatus. It will be the 3rd attempt. This time we will choose the EC as the following Fig. 2.10 shows:

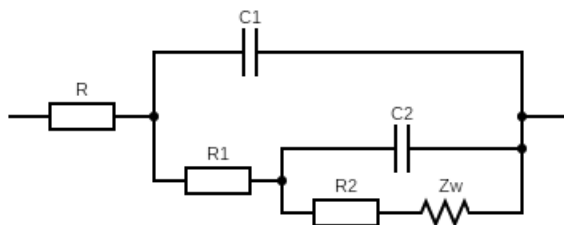


Fig. 2.10 The 3rd EC we choose.

And now we test with this 3rd EC on our data, we got the result shown at Fig. 2.11:

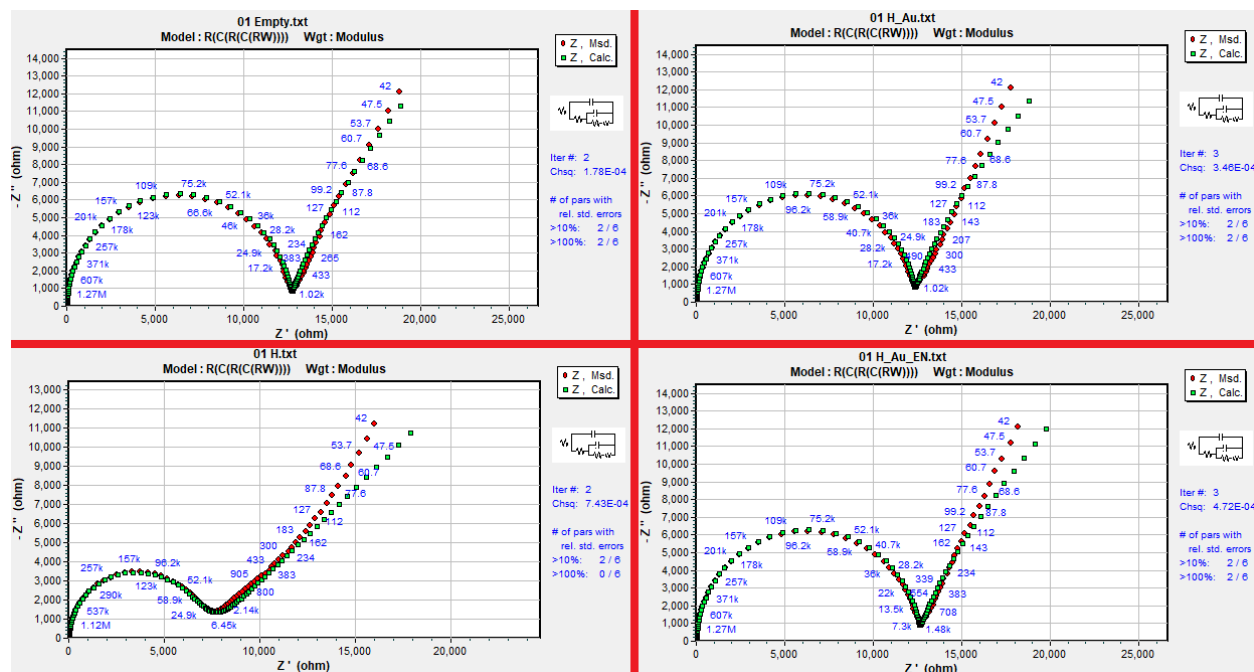


Fig. 2.11 The 3rd EC applied on the Empty Sensor (top-left), with H-DND (bottom-left), with H-DND+AuNP (top-right) and with the H-DND+AuNP+EN drugs (bottom-right).

To be honest, with this EC, our Chsq is not smaller than the 2nd one shown above, but this EC has the minimum variance in comparison with the other two, so it is very stable.

So among the 3 types of EC we chose, the 3rd one is the most suitable, its average Chsq is 4.34E-4, which is 11% better than the 2nd one.

However, as we discussed before, there is no such an EC can satisfy any case, and by adding more apparatus, the result seems to be always improving, but most of the case is not significantly.

In order to confirm this, here we will introduce the last EC, which is even more complex, with extra apparatus, as following Fig. 2.12 shows:

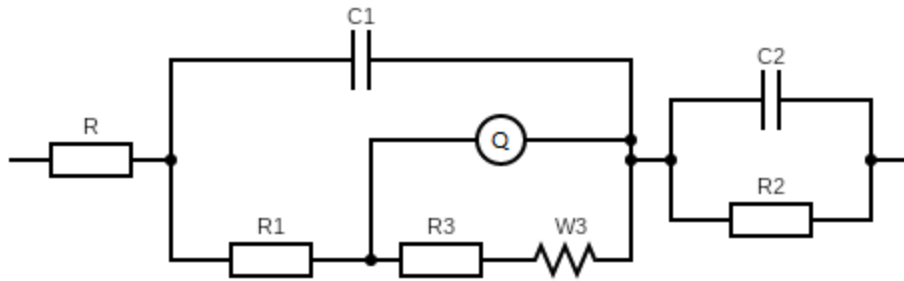


Fig. 2.12 The 4th EC we choose.

With this EC, we can apply it on the given data, here we just pick one of the results as an example, plotted in Fig. 2.13:

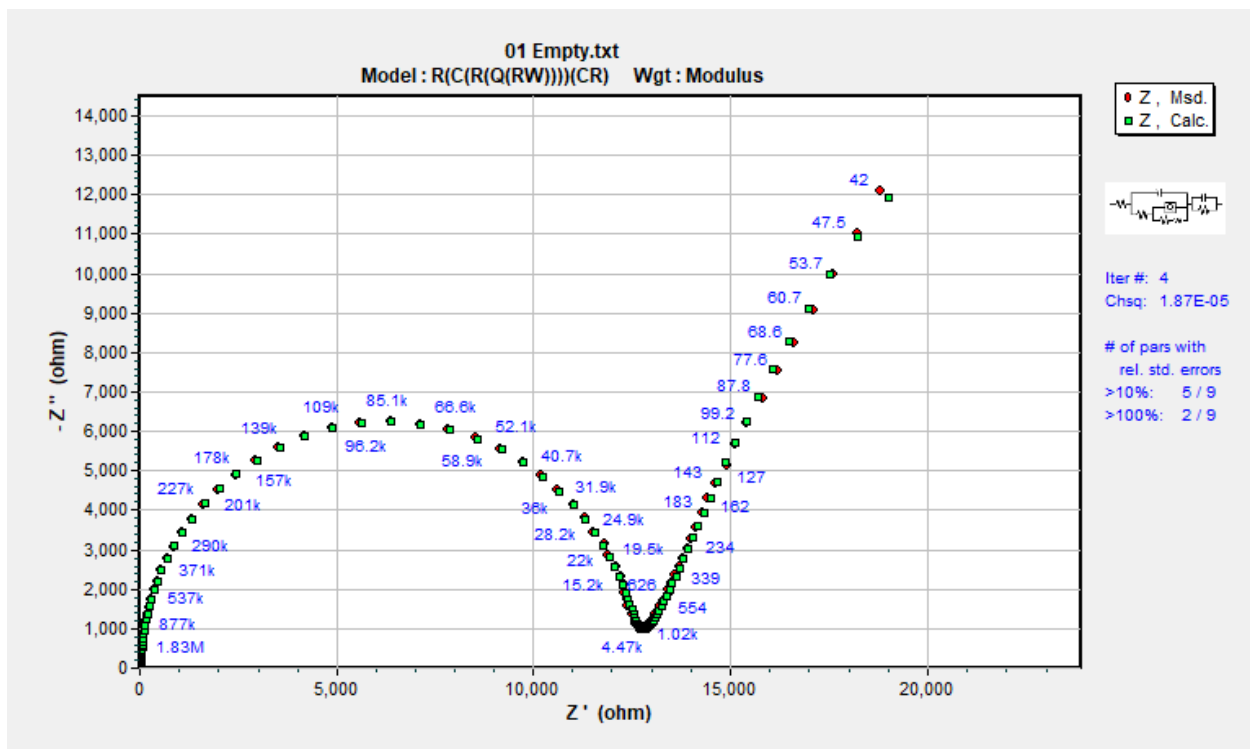


Fig. 2.13 The 4th EC applied on the Empty Sensor 01, we have a very nice result.

As we can read from the figure, this EC provides an even better result, among 4 measurements, its average Chsq is 1.82E-5, almost 10 times better than the third one we took.

However, this EC includes so many apparatus, including 4 resistors, 2 capacitors, 1 Warburg impedance, and 1 Constant Phase Element (Note as Q in Fig. 2.12). These apparatus can help the result to be more and more close to the original data. It can behave even better in the other data, here we do not repeat the procedure, and will save it for the later discussion.

So basically, as we keep adding more apparatus, the result could be improving. Since we have this conclusion, we can finish the test on this software and use another software to see how does it will work.

2.4 Analysis via software EIS Spectrum Analyser v1.0

Now we will introduce our second free software called EIS Spectrum Analyser version v1.0. This software is a standalone program for analysis and simulation of impedance spectra.

The analyzer routine is based on algorithms of the PDEIS spectrometer. In the original (potentiodynamic) version the impedance data analysis is applied on a 3D spectrum and gives dependences of the ac response components on electrode potential. This standalone program has been adapted to solve a wide range of tasks in the common (stationary) impedance spectroscopy, and it is free for non-commercial use.[18]

Generally, it looks like this, as Fig.2.14 shows:

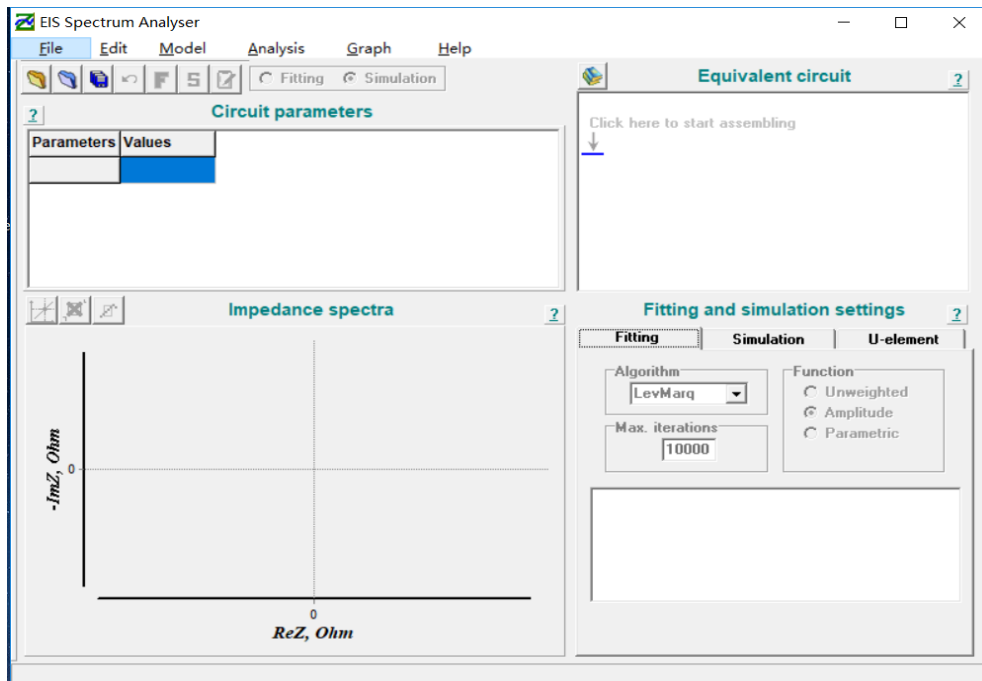


Fig. 2.14 Homepage of the EIS Spectrum Analyser.

The structure and layout are quite similar to ZSimpWin, the biggest difference is in the EIS Spectrum Analyser it has a smaller area of the graph but a larger area for the EC. Others are not that significantly different.

In order to compare the advantages and disadvantages respectively for this 2 software, we will use the same set of data and the same EC for fitting. However, once we load the data file, it shows:

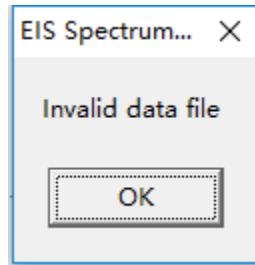


Fig. 2.15 While loading the 1st data, Empty Sensor 01 for the first time.

And we found out, that this software doesn't know what is the length of the data, so it required to put the length of the data as the 1st number in the file. The author seems doesn't want to add one line of code to count the length of the input file. Thus, we have to edit our data, add 100 in each file. Because as we discussed in Chapter 2.2, we have 100 different frequencies.

Once we edit it, we got the following graph:

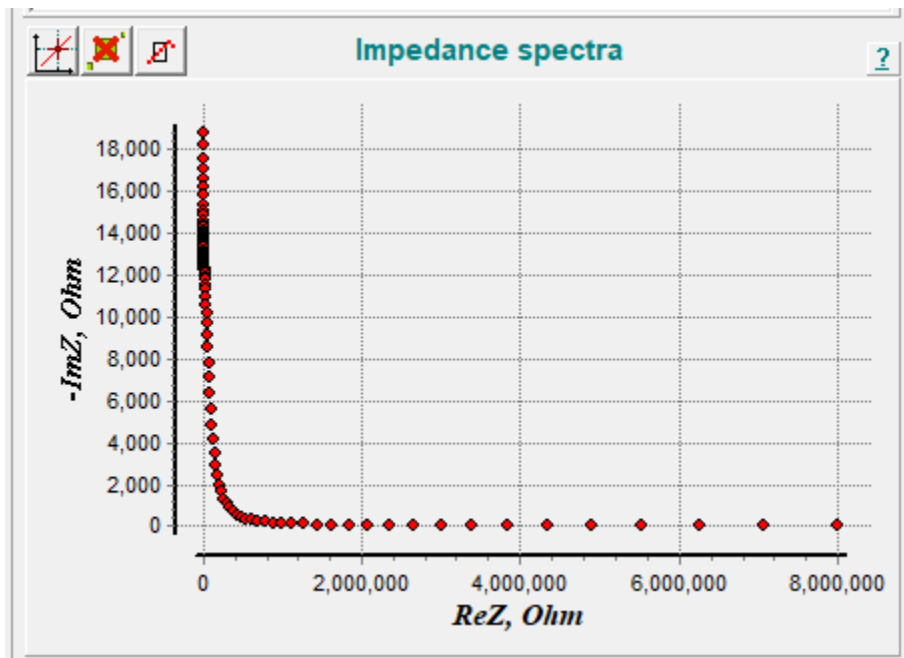


Fig. 2.16 While loading the 1st data, Empty Sensor 01 for the second time, after adding the length.

Which is weird. By reading the axis, we can find out that the X-axis is noted as ReZ , which obviously means the real part of the impedance. But the value is from 0 to 8000000, which is our frequency. So it is clear that the software used our frequency as the real part of the impedance, and used our Z_{Re} as the Z_{Im} , sounds like a total mess. After searching the program toolbar, there is nothing helpful to load our data properly, so we have to reshape our data a bit.

There were 3 columns, Frequency, Z_{Re} , and Z_{Im} . Now we will manually move the sequence as Z_{Re} , Z_{Im} , and Frequency. So the third time we load the data again, we got this figure shown in Fig. 2.17:

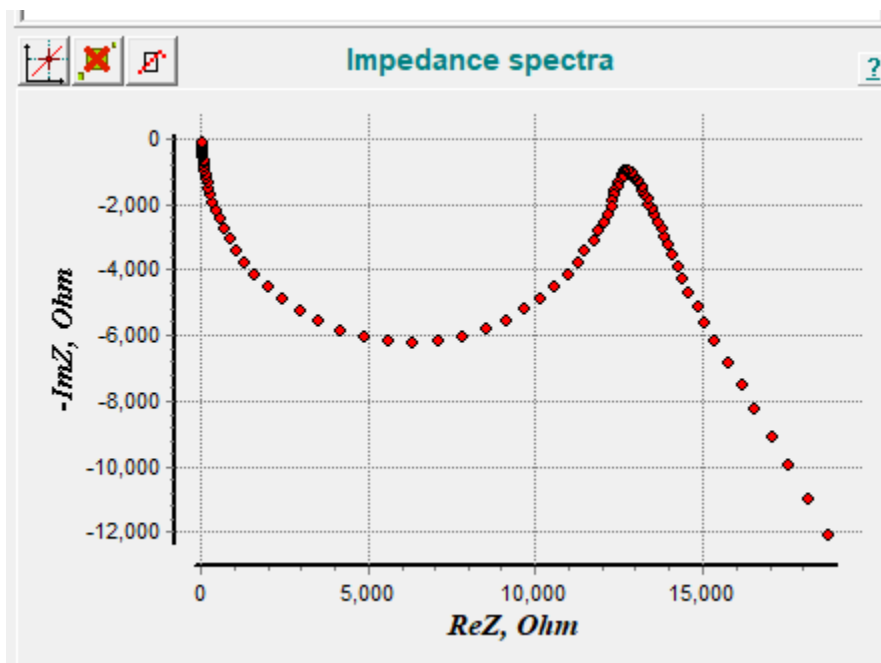


Fig. 2.17 While loading the 1st data, Empty Sensor 01 for the third time, after adding the length and change the data structure.

For some reason, the graph looks like being symmetrized by a line in parallel with X-axis. How it can happen? By reading the graph carefully again, we found out that the Y-axis is not as same as the ZSimpWin software. The Y-axis is the negative of the imaginary part of the impedance, so what we need to do, is to multiply our imaginary data by -1, to make it positive and then, the shape of the graph displayed in Fig. 2.18 will be the same as we saw in Fig. 2.1. So we will do the last change of the data (really the last time), if it will not work, we will uninstall it.

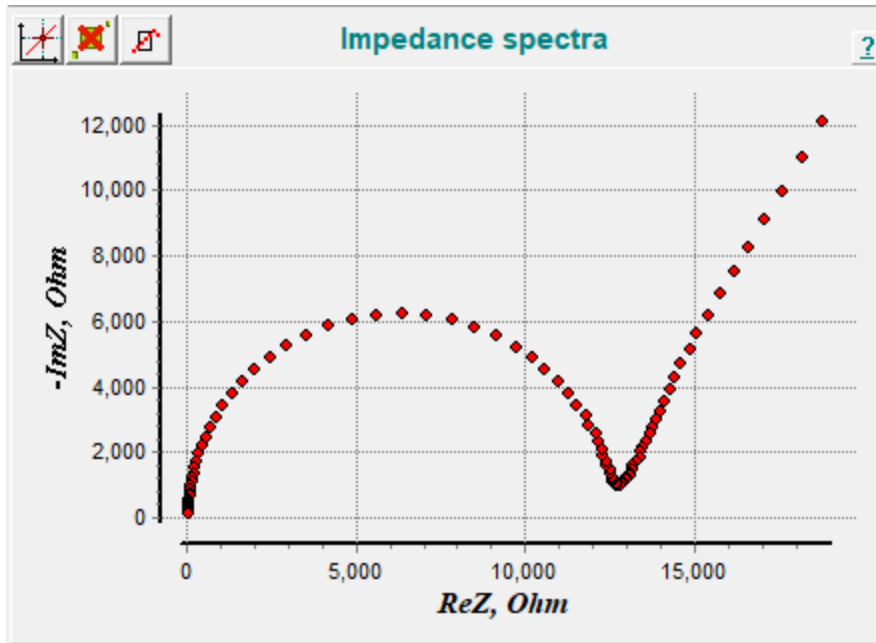


Fig. 2.18 While loading the 1st data, Empty Sensor 01 for the third time, after adding the length and change the data structure.

As we can see from the above graph, luckily, and finally, it looks normal, so we don't have to uninstall it and use a new one, however, the user experience is still very bad, we will discuss it in the following chapter.

Now it's our time to process the data. We will apply those 3 EC shown in Fig. 2.4, Fig. 2.7 and Fig. 2.10 on this data, to see the result.

Before that, we need to declare, that due to the limitation of the length of the thesis, we will not introduce the function of the software in details, and will not display all the result of our test, same as we did in Chapter 2, we will pick up only a few significant results to display here, and we will talk in details about the difference between the original and the fitted data. However, we will still go through all the data behind this thesis.

The first EC we are going to use is Randles EC, which can be found in Fig. 2.4. Here is the result displayed in Fig. 2.19:

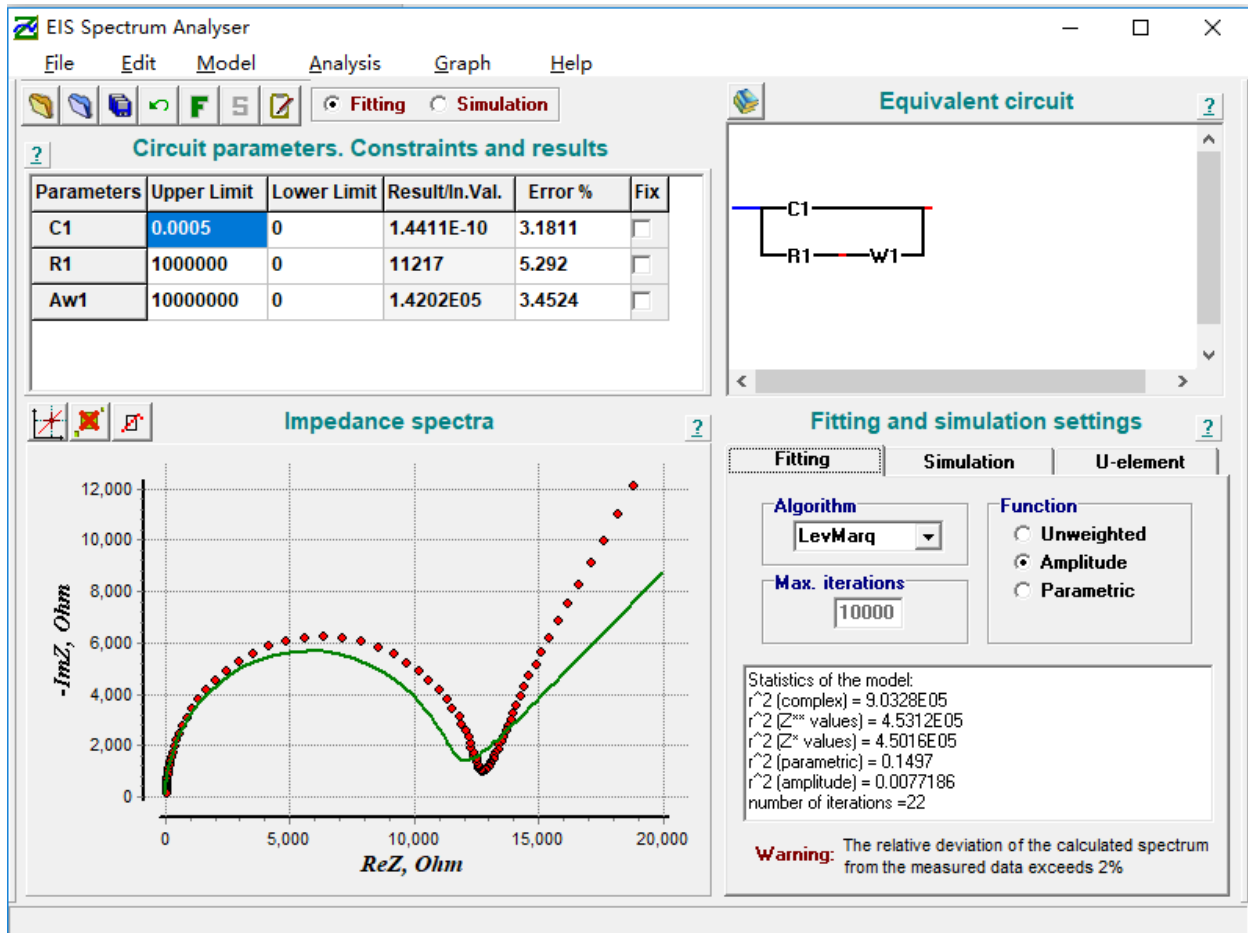


Fig. 2.19 Applying the 1st EC on 01 Empty.

From this figure, we can see it intuitively that it is similar to the result we obtained on Fig. 2.6, which is reasonable because the data and the EC are the same, but the fitting algorithms are different. In this EIS Spectrum Analyser, the default algorithm is the Levenberg–Marquardt algorithm, in the ZSimpWin, was the same. And there are more algorithms like Newton’s method, here we don’t treat it as a primary issue.

With the same idea, we will apply our EC on the rest 3 tests done by sensor 01. The results are displayed in the following Fig. 2.20:

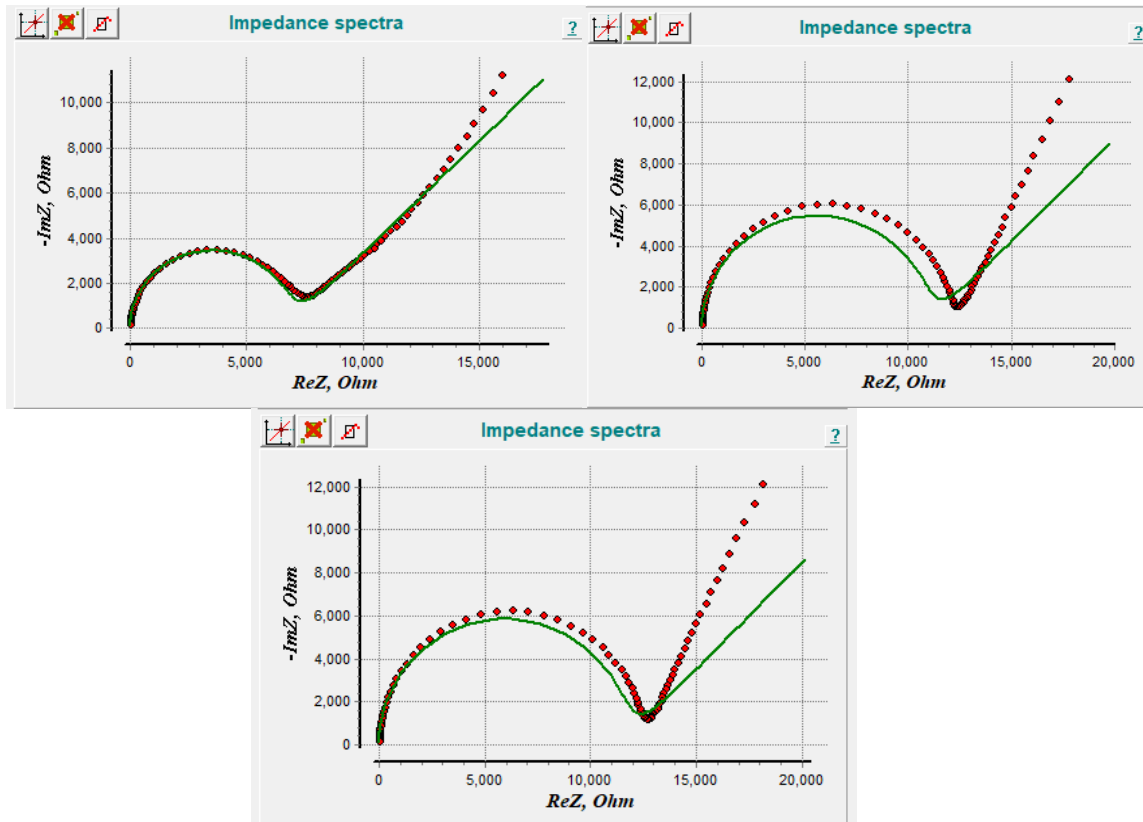


Fig. 2.20 Applying the 1st EC on 01 H (left top), 01 H_Au (right top) and 01 H_Au_EN (bottom).

In this software, it does not present the total error (the difference between the original data and the fitted data), so we will discuss the error separately in the next Chapter.

The rest 2 EC we were applied to data 1 on ZSimpWin will be demonstrated together in the following figures. The second and third EC is shown in Fig. 2.7 and Fig. 2.10, we will apply them on the data again, and we will obtain the result as the following graph shown in Fig. 2.21 and Fig. 2.22:

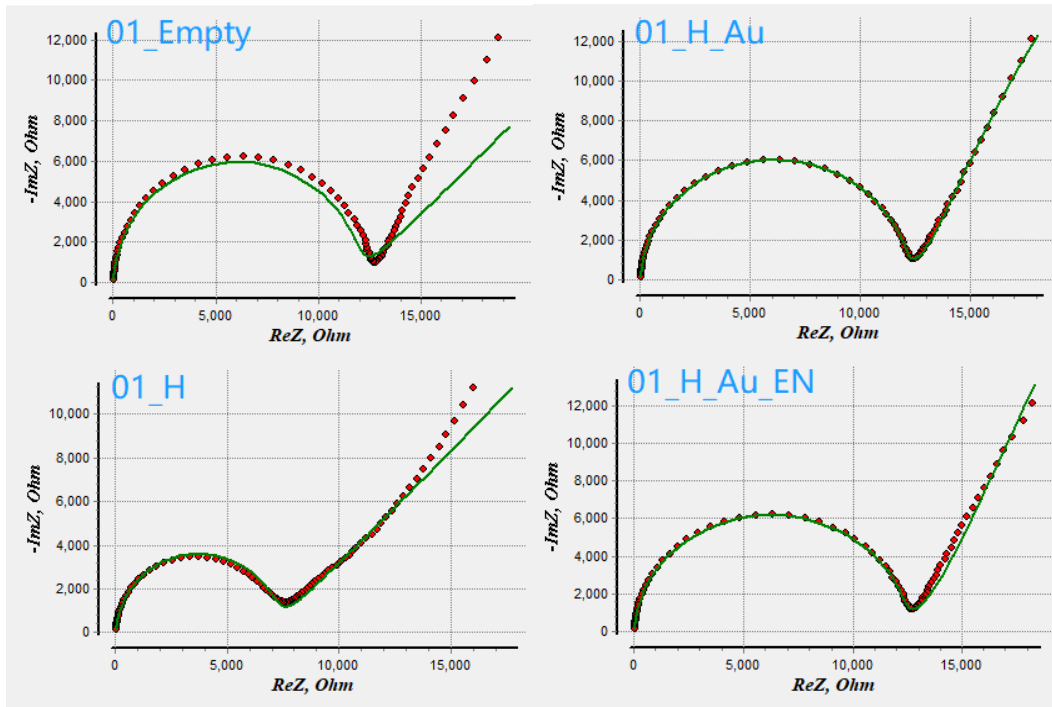


Fig. 2.21 Applying the 2nd EC on 01 Empty (left top), 01 H (left bottom), 01 H_Au (right top) and 01 H_Au_EN (right-bottom).

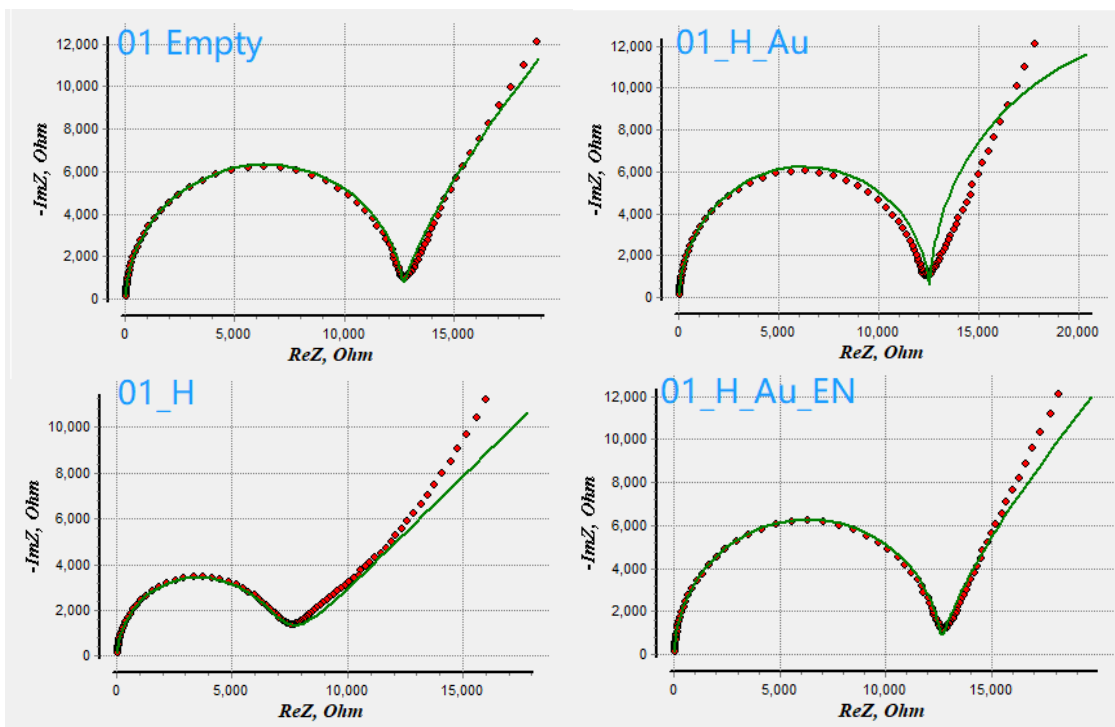


Fig. 2.22 Applying the 3rd EC on 01 Empty (left top), 01 H (left bottom), 01 H_Au (right top) and 01 H_Au_EN (right-bottom).

Till now, we have already learned the basic features of this 2 software, and have some ideas about how does it work and how the results look like while using same data on the same ECs individually.

About the discussion about the obtained results, including the results which was omitted and did not demonstrate here in this chapter, we will keep them for the next chapter, and we will compare them to draw a conclusion.

Chapter 3: Comparison of the results

3.1 Introduction

So we will demonstrate our results from this 2 software, here the result does not mean the value of each EC component which we are not interested in; We need to tell which software is better, so in this thesis, we are focusing on the difference between the fitted data and the original data, as a tool to check how good do the results look. Here we will introduce the following formula (7):

$$\varepsilon = \frac{\sum_{i=1}^n |Z_{Re'i} - Z_{Re_i}| + \sum_{j=1}^n |Z_{Im'j} - Z_{Im_j}|}{n} \quad (7)$$

Here the error is denoted as ε , the $Z_{Re'}$ stands for the real part of the Impedance in the fitted data meanwhile the Z_{Re} stands for the real part of the Impedance in the original data; The $Z_{Im'}$ stands for the imaginary part of the Impedance in the fitted data meanwhile the Z_{Im} stands for the real part of the Impedance in the original data. n is the size of the data, in our case $n=100$ since we have 100 frequencies.

The meaning of this formula is for each frequency, we first take the difference between the real part and the imaginary part separately from original data and the fitted data; Then, we take the absolute value of them, and sum it up. Lastly, we divided the result by the size of the data, so we obtain the so-called Mean Absolute Error (MAE). [19]

So the idea of this formula is to calculate the MAE between the original and fitted data, its advantage is the MAE can avoid the problem that the errors cancel each other out, so it can accurately reflect the actual prediction error. In our case, it expresses how far is the fitted data to the original data we expect the result will be as small as possible – the smaller the error, the perfect the result.

Thus, in the following content of this chapter, for each EC, we will use this formula to calculate the MAE of the obtained data in this 2 software, so we can compare which one is better.

3.2 Result from the Software

We used 3 different EC. For each EC, there are 8 measurements need to go through, each measurement has 4 coatings, calculated by 2 software, so in total, we will have 192 data, which equals to 192 results. But limited by the length of the thesis, we will select half of them to demonstrate.

The data we will use is 01, 02, 03, 05 and 08. As we said before, except the sensors are different in each measurement, another important fact is the difference between the concentration of the EN drug in each measurement.

Thus we will take the EN drug's concentration as 200% (01), 100% (02), 50% (03), 10% (05) and 2% (08), which probably can provide us a significant difference if there will be something related to the concentration.

Now we'll start the process. As we were doing the test in that 2 software in Chapter 2, the thing we are going to do now is to apply the result into our formula above, and list it in Tab. 3.1:

| ZSimpWin Demo 3.30d | | | | | EIS Spectrum Analyser v1.0 | | | | |
|---------------------|------------|--------|--------|--------|----------------------------|------------|--------|--------|--------|
| | | 1st EC | 2nd EC | 3rd EC | | | 1st EC | 2nd EC | 3rd EC |
| | 01 Empty | 741.7 | 54.9 | 167 | | 01 Empty | 720.8 | 695 | 166 |
| | 01 H | 307.1 | 344.9 | 243.1 | | 01 H | 305 | 342.4 | 251.7 |
| | 01 H_Au | 715.8 | 59.7 | 238 | | 01 H_Au | 644.6 | 622 | 173.2 |
| 200.00% | 01 H_Au_EN | 763.7 | 150 | 271.6 | 200.00% | 01 H_Au_EN | 758 | 732.8 | 274.7 |
| | | | | | | | | | |
| | 02 Empty | 654.7 | 82 | 173.8 | | 02 Empty | 644.8 | 621.9 | 172.9 |
| | 02 H | 324.7 | 357.7 | 268.3 | | 02 H | 328.4 | 189.6 | 328.4 |
| | 02 H_Au | 573.4 | 68.9 | 579.3 | | 02 H_Au | 566.6 | 545.2 | 264.8 |
| 100.00% | 02 H_Au_EN | 623.6 | 108.1 | 256 | 100.00% | 02 H_Au_EN | 618 | 595.3 | 615.6 |
| | | | | | | | | | |
| | 03 Empty | 705 | 99.6 | 199.5 | | 03 Empty | 694.4 | 461 | 198.6 |
| | 03 H | 318.8 | 3667.7 | 285.5 | | 03 H | 1818.2 | 1583.3 | 327.3 |
| | 03 H_Au | 541 | 48.8 | 204 | | 03 H_Au | 531.6 | 510.9 | 203.4 |
| 50.00% | 03 H_Au_EN | 596.7 | 80 | 214.5 | 50.00% | 03 H_Au_EN | 589.4 | 567.9 | 215.8 |
| | | | | | | | | | |
| | 05 Empty | 587.9 | 59 | 167.3 | | 05 Empty | 575.3 | 553.4 | 166.5 |
| | 05 H | 416 | 155.5 | 377.6 | | 05 H | 419.2 | 417.3 | 379.1 |
| | 05 H_Au | 535.5 | 56.2 | 161.8 | | 05 H_Au | 524.1 | 503.6 | 161.4 |
| 10.00% | 05 H_Au_EN | 598.3 | 70.5 | 184.3 | 10.00% | 05 H_Au_EN | 589.3 | 610 | 189.7 |
| | | | | | | | | | |
| | 08 Empty | 608.7 | 37.8 | 165.7 | | 08 Empty | 545.9 | 575.3 | 165 |
| | 08 H | 384.9 | 413 | 384.9 | | 08 H | 376.1 | 405 | 376.1 |
| | 08 H_Au | 515.7 | 67.8 | 212.4 | | 08 H_Au | 509.5 | 489.8 | 221.5 |
| 2.00% | 08 H_Au_EN | 540 | 53.41 | 207.3 | 2.00% | 08 H_Au_EN | 533.7 | 513.4 | 215 |

Tab. 3.1 The result of the MAE in from each software in each EC of each measurement.

Here we will describe a little bit, from the Tab. 3.1, the left part colored into pink is the result from the ZSimpWin Demo 3.30d, the right part colored into the blue is the result from the EIS Spectrum Analyser v1.0. For each measurement, we take the 4 coatings and test them with those 3 different EC we've mentioned via 2 software, one after another. The concentration of EN drugs has been placed next to them. The value in the table is the MAE calculated by the formula (7).

3.3 Comparison and Discussion

Now, we can see a lot of difference between the MAE of our results from this 2 software:

Generally, the left area has significantly smaller errors compare with the right part; In some cells, the difference of the error is very large.

The trend of the MAE is going down when the concentration of the EN drugs is going down. And, the 1st EC looks like the worst one, because it has the largest error compare with the other 2; The 2nd EC is roughly better than the 3rd one in some case, but in the other case not.

However, in some cells, the MAE is unexpected very large, some of them are over 1000 and even over 3000. We will take one example to discuss:

The data 03 H, with 2nd EC, the MAE is 3667.7, which we can see from the plot in the following Fig. 3.1:

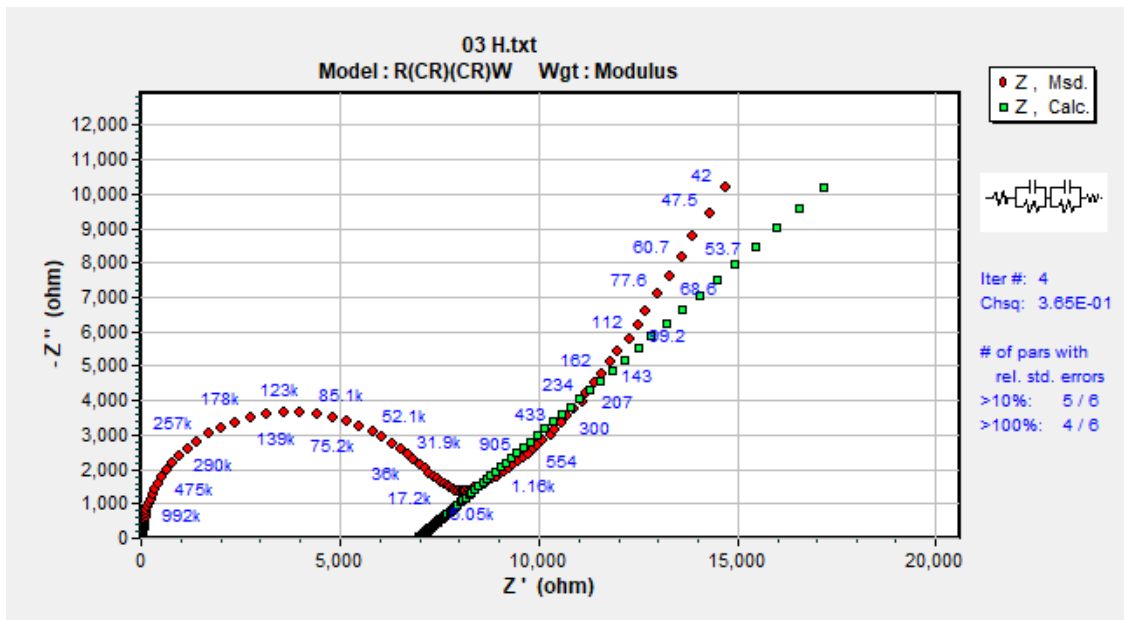


Fig. 3.1 Plot of the 03 H with the 2nd EC.

As we can see from this figure, the fitting is such a mess, the ChSq is very large, so there must be some parts went wrong. But this software doesn't tell us where, so we will use something like a binary search, which means we will divide the data into 2 parts (half-half) since the size is 100, then the size of each part is 50. We will plot them separately in Fig. 3.2:

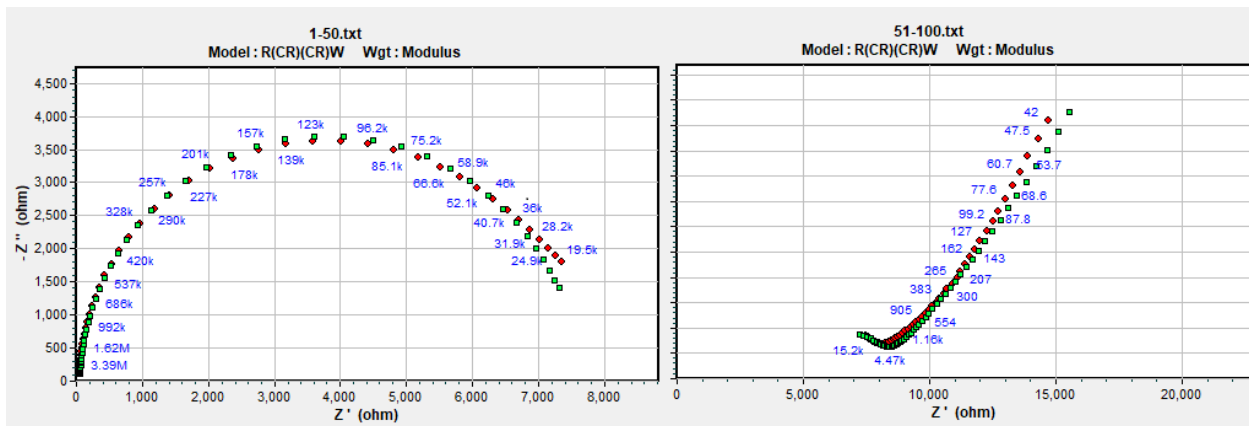


Fig. 3.2 Plot of the 03 H with the 2nd EC divided into 2 parts.

So we can see that the left one seems to be ok, but the right one, although it looks like fitted, the left edge is still messy. We will go deeper into the right one, which we will divide them into half-half again, shown in Fig. 3.3:

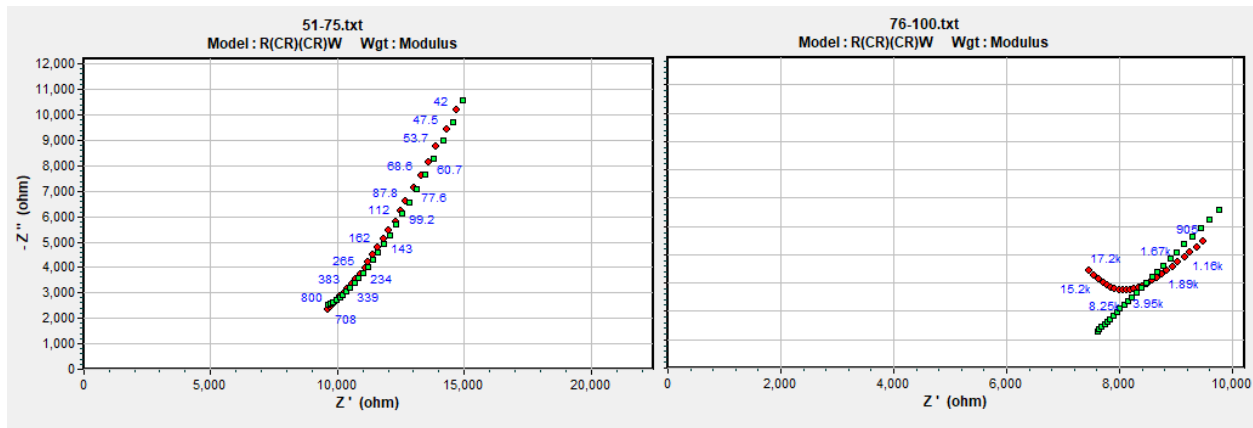


Fig. 3.3 Plot of the right part of Fig. 3.2 divided into 2 parts.

Now is pretty clear. The problem happens in the frequency range from 905-15200 Hz, as it shows in Fig. 3.3. But, we cannot divide it again into half, because the software requires the minimum size of the input data is 15. However, it is still enough for us to point out, that part is non-linear, which the software cannot easily deal with. This problem may come from the measurement, like the sensor might be polluted, or due to some other reason which may interfere with our result.

After our observation, we finally can make several conclusions from what we have learned above.

Chapter 4: Conclusion and discussion

4.1 Discussion of the software

Now it's time to announce which software is better. Based on the function, work efficiency, convenience, accuracy, stabilize, GUI and user experience, the 1st software, ZSimpWin (ZSW), has significant advantages than the 2nd one, EIS Spectrum Analyser (SA).

First is about its function. In the ZSW, it definitely has more function than the SA, especially we can find the necessary explanation easily in the documentation. Meanwhile, the SA has less function and the documentation is sometimes not described well.

Work efficiency, it is hard to say which one is better, because in our case, all the computation could be finished with 2 seconds, so we don't need to distinct it now.

Talking about the convenience, actually, both of them are really bad, a lot of things we have to do it manually, but the SA is the worst one because it requires us to change the sequence of the data, and add the size of the data. ZSW obviously used several lines of code to solve this issue. This is exactly what user prefer: we don't have to adapt to it, but it will adapt to us.

Then, the accuracy is also important. As Tab. 3.1 shows, ZSW has relatively overall less error in comparison with SA while dealing with the same data, but not in all case, sometimes the SA is not that bad, and can perform good result also.

Moreover, The result and the MAE from the SA are not very stable compared with the ZSW, by reading its documentation, we can learn that it uses four different algorithms to process the data: Levenberg–Marquardt Algorithm (default), Nelder-Mead Simplex Method, Powell's method and Newton's method. In reality, we have to choose the algorithm manually, where the ZSW software will choose it automatically, especially in the case that the default software doesn't work.

The graphical user interface of this 2 software, the ZSW is still better, especially the expression of the EC, it at least uses the readable chart to express; Meanwhile, the SA just use several letters which looks very cheap.

Last but not least, the user experience is quite bad. Especially the SA, every time if you need to input some data, you have to transform it first, otherwise it will show the I/O error. To transform the data, and then used in the SA, which wastes quite a lot of time.

In general, we cannot demand too much since they are just free software, although its paid version does not worth its price, the software is still a powerful tool for us to use. If it can provide the function for dealing with the non-linear case, and improve the I/O interface so that the user can manipulate the data as a group, but not one by one, that will be great.

4.2 General conclusion and discussion

As we observed in Fig. 2.9, 2.11, 2.20, 2.21, the shape of the graphs looks different while applied with four different substances (Empty sensor, H-DND, AuNP, and EN drugs). Especially, the resulting graph of the H-DND is the most different compared with the other three, and it is also the problematic one while doing the fitting as we discussed in Chapter 3. But, thinking about the different coating, they were added one after another, the graphs behave like “Normal, Abnormal, Normal, Normal” which mapped to these four substances (Here, the normal means it somehow looks similar to the Fig. 1.12, which is the ideal figure after the calculation).

The interesting part is, it is clearly shown that the resulting graph looks better after we add the AuNP, so we can propose that the AuNP actually helps to stabilize the result, which probably caused by H-DND itself, as we've mentioned in Chapter 1.3.

As we can see in Chapter 2, the 3 EC we used has gradually become more and more complex, with more and more apparatus, together with our result, we can draw a conclusion:

It is not 100% true that the more apparatus we use, the more precise our result will be. However, if we use a small number of limited kinds of apparatus only, we will never approach a good result, as we can learn from Chapter 2.3, the Randles Circuit is not working for all the cases, not only because of the measurement, but more related its simplest structure.

Moreover, with this conclusion, by adding more complex apparatus, we find out that there is several apparatus helped a lot during the calculation and fitting. With these units, the fitted data has less error compare with the originals, we can point out some like Warburg Impedance and the Constant Phase Element (CPE), although it is not demonstrated so much in Chapter 2 and 3 during the length limit of this thesis.

Another knowledge we can learn from Tab. 3.1, is the influence of the concentration. So far as we can see, the lower the concentration, the lessor the error, the more accuracy we will have; And it seems also influenced by the kinds of substance we used for the test: The more coatings we have (the more different kinds of substance we applied on the sensor), the larger the error we will obtain.

This reminds us of the similar structure of the increasing of the entropy: The higher the entropy, the larger the mess/disorder in the system.

So overall, we could not rely on this software that much, because at least according to this 2 software, it cannot perform the nearly “perfect” results, because it could not deal with the non-linear part easily. And under the shortage that it has a limited number of ECs, it doesn’t help us to choose the EC, in other word, we have to choose the best suit EC manually.

However, it is still recommended to use the software first, because at least it can be very useful, faster and easier to manipulate with the given several data, for checking the trend as a reference for us to think about an optimal way to solve it and write some code to make the result even better.

For some data, the software could have a smaller error which means a nice result, but for some other data, the software can be totally useless, while dealing with the non-linear case. So, there isn’t exist such software which can satisfy all the cases. That’s why plenty of the scientific papers did not mention which software they were using for processing the data.

Last but not least, after we compared the advantages and disadvantages of the software, we have learned how to describe and analyze the mathematical model of impedance characteristics of nanoparticle covered interdigitated sensors.

But what about the mathematical model itself? Or, the basis of the model, which is the EC we used while processing the data?

The answer or the discussion will not be ended in this thesis, because as we have mentioned above, about how to the EC logically or what rule should we follow, looks like a black box in front of us. No one knows why, and no one knows how. We just know, by using several kinds of EC, together with the suitable algorithm, sometimes it works, and sometimes it's not.

We don't know what it's behind. It does not fully represent the physical reality, it is just an approximation. We cannot control what will happen, but we are doing our best to improve it.

Here we use a famous quote as the ending of this thesis:

“As far as the laws of mathematics refer to reality, they are not certain; and as far as they are certain, they do not refer to reality.”

--- Albert Einstein (1879 - 1955)

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