

Impedance Spectroscopy: Fundamentals and Applications

G. Fafilek^{a*}

^a Institute of Chemical Technologies, TU Wien, Getreidemarkt 9/164ec
*guenter.fafilek@tuwien.ac.at

Electrochemical impedance spectroscopy is a versatile tool for the characterization of materials and electrochemical processes. It provides a detailed insight into the electrical properties of electrochemical systems or even physicochemical processes like mass transport phenomena connected to Faradaic processes.

On one hand – technically – it is a simple method widely used in battery and fuel cell research, corrosion science and other fields of electrochemistry. However, on the other hand, since specific impedance data is not exclusively connected to specific processes, the physical interpretation of impedance spectra is challenging.

The “impedance” is the ratio between a voltage across a component and the electrical current flowing through it.

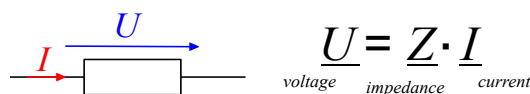


Fig. 1 Relation between alternating current and voltage for a component resembling Ohm's law.

The value for the impedance at a certain frequency of a sine-wave shaped AC signal is a complex number. Considering the impedance in terms of absolute value (or modulus) and phase angle, the modulus reflects the ratio between the amplitudes of the voltage and the current, like it is the case in Ohm's law for ohmic resistors. However, some basic electrical elements, like capacitors or inductors, behave like small energy storage elements, and therefore for them, Ohm's law is not valid at all times. This behaviour causes – for sine-waves – a phase shift between current and voltage. The phase angle of the complex value for the impedance is identical to this phase shift. For the impedance of a mixed network consisting of resistors and capacitors (or other AC elements), modulus and phase angles are frequency dependent. The frequency dependence of a system is a kind of “fingerprint” for the occurring processes.

This contribution shows the mathematical origins of the concept “impedance” and derive the basics of the “golden rules” to be followed when measuring impedance.

These are → make sure that your system fulfils:

- linearity
- stability
- causality

which is difficult to achieve in electrochemical systems. Electrochemical processes are strongly non-linear, which means that Ohm's law ($U = I \cdot R$) does not apply in general. Moreover, such systems are not stable, e.g. a corroding surface changes its properties over time or a battery might change its state of charge during a measurement. The third condition “causality” might be violated by external sources of signals e.g. noise.

The first step in making good impedance measurements is to build a suitable measuring setup. The most important rule is shielding to avoid external noise. Use short cables to reduce inductive effects and again noise. When using 3 electrodes, like it is often the case in electrochemical setups, additional complications arise from the bandwidth of the potentiostat and from coupling effects between the electrodes.

Since the system can be non-linear, low signal amplitudes have to be used. It is very common to apply a voltage with just 5mV amplitude to avoid non-linear current response. In this case, the signal to noise ratio might become an issue.

If stability could be a problem, the data can be checked with the Kramers-Kronig-relation. Modulus and phase or real and imaginary part of the complex impedance cannot change independently with frequency. The KK-relation checks if these values correlate correctly and if not, stability might be a problem. As an example, a pure ohmic resistor has phase angle of 0 degree and a frequency independent modulus. If the resistor changes with time (the system is not stable), a change of the modulus with frequency is observed because each measured data point corresponds to a different point in time. The KK-test detects such, even less obvious, inconsistencies.

Once valid impedance data is available, in most cases it can be related to the behaviour of an electrical equivalent circuit. Selecting a suitable equivalent circuit is the second step in successfully analysing the impedance of a system. Theoretically, an impedance spectrum can always be described by an equivalent circuit, provided it is sufficiently complicated. The challenge is to find a circuit of which the elements can be related to electrochemical or physical processes.

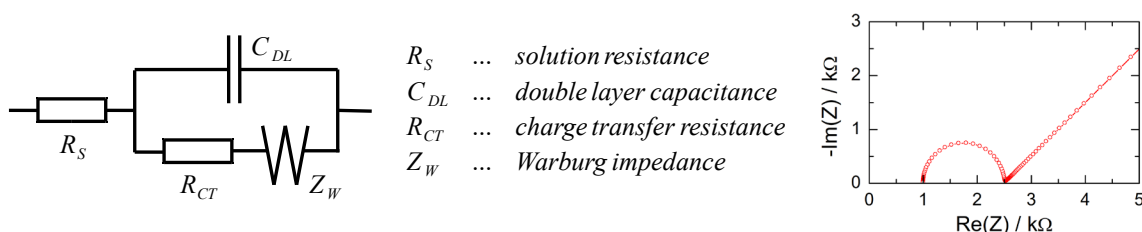


Fig. 2 Randles equivalent circuit [1] with the denotation of each element and the complex plane plot of the corresponding impedance spectrum.

The most common circuit, which describes the behaviour of an electrode is the Randles equivalent circuit displayed in Fig. 2. It includes the properties of the interface between the electronic conductor (the electrode) and the ionic conductor (the electrolyte solution), consisting of the double layer capacity (C_{DL}) and the resistance of the double layer (R_{CT}) against the charge transfer reaction which is the redox reaction of an electroactive species (a Faraday reaction). Limited mass transport by diffusion is described with the Warburg impedance Z_W . The Warburg impedance is a specific combination of resistive and capacitive (storage) elements in a “transmission line”. R_s represents the solution resistance of the cell.

Such simple equivalent circuits are only valid for “simple systems”. This means for instance that a one-dimensional geometry has to be assumed. However, real systems do not have a one-dimensional geometry, they do have a, sometimes complicated, 3-D geometry on the nano- to macroscopic scale. Real electrodes have roughness, are porous or have certain shapes and arrangements in relation to each other. In addition, the electrical parameters can have a spatial distribution. All these properties influence the impedance spectra, which must be taken into account. In order to include these effects in equivalent circuits, so-called “constant phase elements” CPEs are used. Strictly speaking, resistors and capacitors are also CPEs, with phase angles of 0° and -90° respectively. A general CPE is neither a resistor nor a capacitor, but something in between with a phase angle of $0^\circ > \varphi > -90^\circ$. For example, the double layer capacitance is often described as a CPE with a phase angle close to, but not exactly -90° .

After selecting the proper equivalent circuit diagram for a system, the third step in impedance analysis is to determine the correct values for the elements. For this purpose, a non-linear curve fitting of complex functions with multiple parameter adjustment is performed. Fortunately, there is special software that enables the drawing of electrical circuits and the automatic generation of the impedance function. The program finds minima of the target function, which is the sum of squared differences between measured and calculated data. With complicated circuits, there is a risk of getting stuck in local minima. Good estimates for the initial values are therefore important.

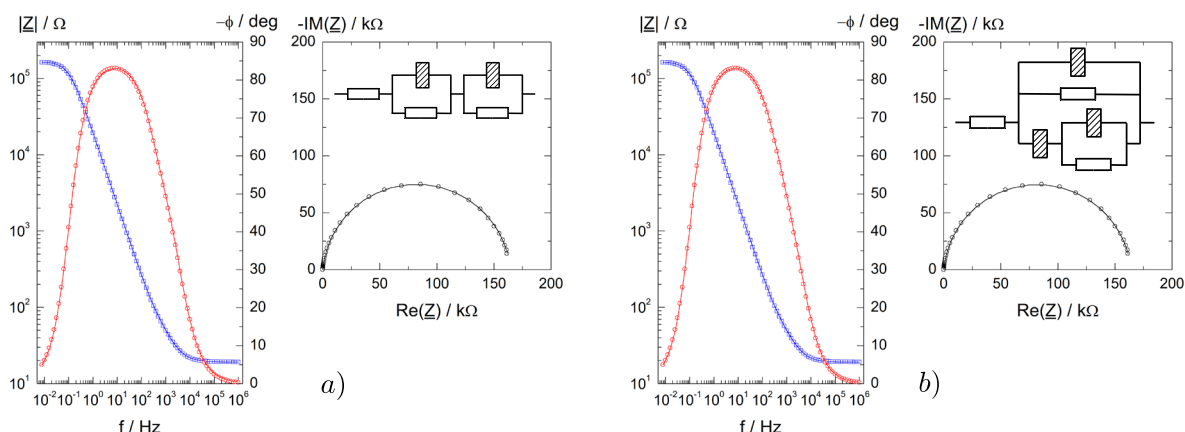


Fig. 3 EIS of a passive layer on Zn (symbols), a) and b) show the simulated impedance (lines) with two different equivalent circuits (inserts). The quality of the fit is practically equal, however model b) better represents the physical properties of the passive layer [2].

In Fig. 3 a comparison is made between two fits with different equivalent circuits representing the impedance of a passive Zn surface. There is practically no difference of the quality of the fit, which shows the difficulties in finding the right model.

If there is a good fit, the story is not over yet. The last step of the procedure is to identify the elements with physical processes. This interpretation of the equivalent circuit is the most important, but also the most difficult part of impedance analysis. It requires additional knowledge of the system, either from experience or from additional experiments, such as independent analytical data or specific electrochemical methods. In some examples it is demonstrated how the interpretation of impedance spectra is possible by varying the experimental conditions. For instance, the model of the example in Fig.3 b) is the better choice, since the parameters change their values correctly with the applied DC-potential.

Acknowledgements

This research was sponsored by the NATO Science for Peace and Security Programme under grant id. G6106.

References

- [1] J. E. B. Randles, "Kinetics of rapid electrode reactions", *Discuss. Faraday Soc.*, vol.1, pp. 11-19, 1947, doi: 10.1039/DF9470100011.
- [2] G. Fafilek, "A novel experimental method for potential controlled electrochemical impedance spectroscopy", *Monatshfte fuer Chemie*, vol.140, pp. 1121-1127, 2009.