

Lecture # 12

The impedance of complex electrochemical systems. Benefits of electrochemical impedance spectroscopy (EIS).

Goal

This lecture provides an advanced understanding of impedance behavior in complex electrochemical systems. Students will explore how EIS can be applied to multi-step reactions, porous electrodes, and composite materials, and how equivalent circuit modeling enables quantitative evaluation of electrochemical and physicochemical processes.

Electrochemical Impedance Spectroscopy (EIS) is a technique that helps us understand how electrochemical processes work — how fast reactions happen, what mechanisms are involved, and how the system behaves overall.

This method is widely used in many areas, such as:

- **corrosion studies** (to understand and prevent metal rusting),
- **semiconductor research**,
- **energy storage and conversion technologies** (like batteries and fuel cells),
- **chemical and biosensors**, and even in **noninvasive medical diagnostics**.

The basic idea is simple: an electrochemical system that is at equilibrium or in a steady state is slightly “disturbed” by applying a small sinusoidal signal (an alternating current or voltage) over a range of frequencies. Then, we measure how the system responds — the resulting current or voltage.

If the system behaves linearly and remains stable over time (meaning its response is proportional to the input and doesn’t change with time), it can be described as a transfer function — showing how the input signal (voltage or current) is transformed into the output signal (current or voltage) at different frequencies.

In simple terms, EIS allows us to “listen” to an electrochemical system at different frequencies to understand what’s happening inside, without damaging it.

The main advantage of Electrochemical Impedance Spectroscopy compared to other electrochemical methods is that it can separate and analyze many different processes happening inside an electrochemical

system at the same time. This gives scientists a lot of detailed information about the electrical, electrochemical, and physical behavior of the system.

An important feature of EIS is that the data obtained from an electrochemical system can be represented as an equivalent electrical circuit. This circuit is made up of ordinary components like resistors, capacitors, and inductors, as well as more complex elements called distributed components, all connected in different ways [1].

In simple terms, each process happening in the electrochemical system — such as charge transfer, diffusion, or double-layer charging — can be thought of as similar to a specific part of an electrical circuit, and each of these parts has its own time constant.

To do this, EIS data are usually fitted or simulated to a model circuit using special software. Most electrochemical analyzers already have built-in programs that allow this kind of simulation. There are also dedicated tools, such as Z_{View} and Z_{Plot} , which are widely used for this purpose [2].

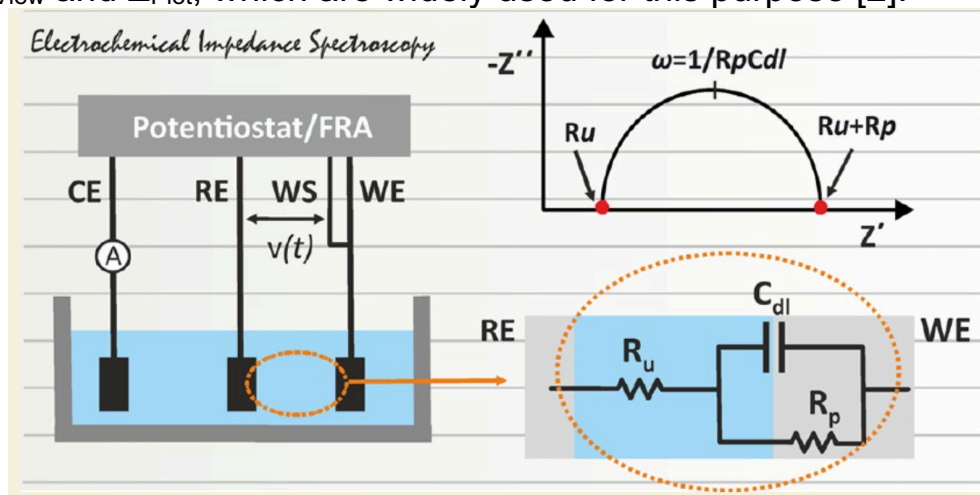


Figure 1. Graphical abstract of method EIS [2].

These unique capabilities have established EIS as a powerful and highly competitive technique for the study, optimization, and development of various real electrochemical cells in modern applications in corrosion science, fuel cells, lithium-ion batteries, photovoltaic cells, and (bio)sensing.

Examples of EIS Applications.

In [3] is shown how magnesium ions (Mg^{2+}) are inserted into titanium dioxide (TiO_2), which is used as an electrode material in rechargeable batteries.

EIS was used for analyzing how easily the ions move inside the material and how the electrolyte (a solution containing LiCl) affects this process.

EIS helped to separate different phenomena — such as **charge transfer** and **ion diffusion** — by identifying their distinct time constants. From the impedance data, they calculated parameters like the **charge transfer rate constant** and **diffusion coefficient**, which revealed that the presence of LiCl improved the Mg^{2+} insertion kinetics (Figure below).

This example shows how EIS can provide detailed kinetic and transport information that is not easily obtained by other electrochemical methods.

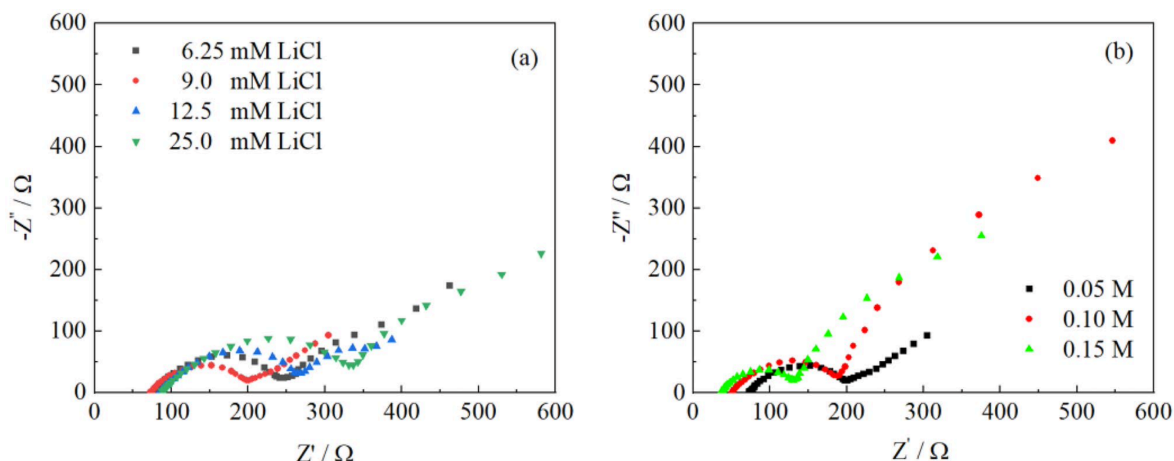


Fig. 5 **a** Nyquist plots of the TiO_2 in 0.05 M $\text{Mg}(\text{ClO}_4)_2$ in AN electrolyte at different concentrations of LiCl. **b** Nyquist plots of the TiO_2 in 9 mM LiCl + AN at different concentrations of $\text{Mg}(\text{ClO}_4)_2$

In another study [4], a composite material made of **polyaniline (PANI)** and **indium oxide** (In_2O_3) was used to detect the drug diclofenac sodium.

EIS was applied to understand the **surface and interface properties** of the modified electrode.

The impedance spectra showed how the composite improved **charge transfer** and **reduced interfacial resistance**, which resulted in higher sensor sensitivity and stability (Figure below).

EIS was essential for optimizing the design of the electrochemical sensor and understanding how the electrode surface behaves during detection.

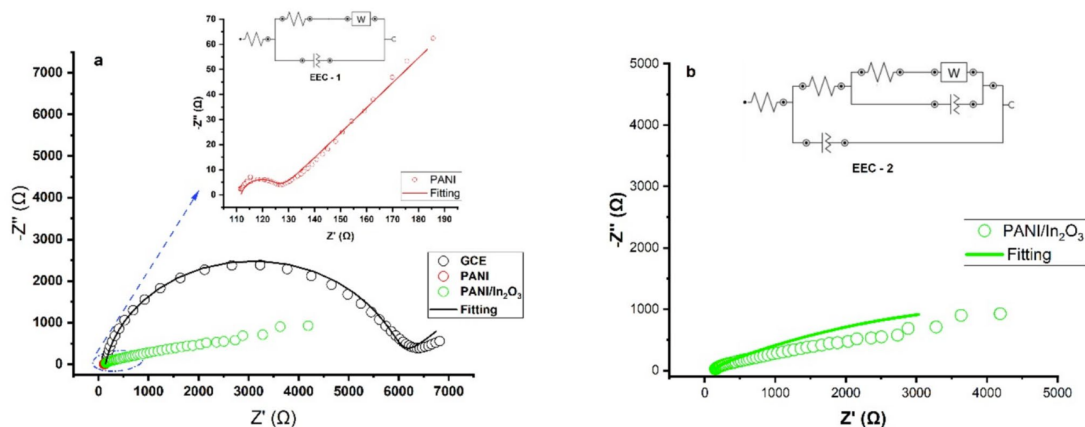


Fig.2 Nyquist plots of the bare GCE, GCE/PANI, and GCE/PANI/In₂O₃ obtained in 0.1 M PBS buffer containing 5.0 mM Fe(CN)₆³⁻/Fe(CN)₆⁴⁻. Insets: **a** Nyquist plots of the GCE/PANI and the electrical equivalent circuit (EEC-1) applied for GCE and GCE/PANI electrodes; **b** the electrical equivalent circuit (EEC-2) applied for GCE/PANI/In₂O₃ electrode

Learning Outcomes

By the end of this lecture, students will be able to:

1. Explain the impedance response of complex systems involving multiple charge transfer and diffusion processes (related to LO 2.2 and 3.1).
2. Apply equivalent circuit and transmission line models to interpret impedance spectra of heterogeneous materials (related to LO 3.1 and 3.3).
3. Evaluate the advantages and limitations of EIS compared to other electrochemical techniques for system diagnostics (related to LO 3.3 and 4.3).

Questions and Self-study Assignments

1. Discuss how impedance responses differ between simple and complex electrochemical systems.
2. Explain the concept of distributed elements and transmission line modeling in EIS.
3. Interpret a Nyquist plot showing multiple semicircles and assign each to a distinct electrochemical process.
4. Compare EIS with cyclic voltammetry in terms of information obtained, time resolution, and diagnostic capability.
5. Review one publication applying EIS to investigate porous electrodes, fuel cells, or coating materials, and summarize its main findings and methodological benefits.

References

1. Bard, Allen J., Larry R. Faulkner, and Henry S. White. Electrochemical methods: fundamentals and applications. John Wiley & Sons, 2022.
2. Alexandros Ch. Lazanas and Mamas I. Prodromidis. "Electrochemical Impedance Spectroscopy - A Tutorial" ACS Meas. Sci. Au 2023, 3, 162–193. <https://doi.org/10.1021/acsmeasuresciau.2c00070>
3. Rakhymbay G., Avchukir K., Konysbay Ye., Vacandio F., Jumanova R., Bakhytzhan Ye., Abildina A., Argimbayeva A. Influence of LiCl on the kinetics of Mg^{2+} insertion into TiO_2 prepared by solid-state chemical reaction //Journal of Solid State Electrochemistry 2023 <https://doi.org/10.1007/s10008-023-05742-0>
4. Rakhymbay. G., Vacandio F., Avchukir K. Using PANI| In_2O_3 composite for indirect electrochemical detection of diclofenac sodium via polyaniline oxidation peak // Electrocatalysis. – 2024. <https://doi.org/10.1007/s12678-024-00914-6>