# In situ diagnostics of electrocatalytic systems by electrochemical impedance spectroscopy

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**Abstract**

The demand for new electrochemical reaction technologies and related engineering aspects is rising due to the current transition to green technologies and to use of renewable electricity sources. In this context, research of new electrocatalytic pathways to improve processes efficiency and reduce their costs is essential. Electrochemical characterizations are usually employed in the study of new electrocatalysts and electrochemical systems. Among them, electrochemical impedance spectroscopy (EIS) is nowadays highly exploited to investigate charges transport and transfer phenomena. Nevertheless, EIS can be used for other purposes as well.

This review will focus on the use of the EIS technique as a diagnostic tool in the electrocatalysis field. Surprisingly, among the numerous electrochemical reactions, the areas in which EIS is employed as a monitoring tool are very few. The most important are the ones with a high technological maturity level and, therefore, that are already employed in the industry or for commercial applications: e.g., batteries, fuel cells and biosensors. Devices belonging to these groups need to control their working conditions with fast and reliable methods, even at the cost of losing a small amount of precision degree. In this perspective, EIS is often used in combination with machine learning algorithms to develop easy-to-use diagnostic devices that aim to a rapid indication of the system status rather than a precise understanding of all the underlying processes.

**Keywords**

Electrochemical Impedance Spectroscopy, electrocatalysis, diagnostic tool, electrochemical cell, machine learning

## Introduction

With quickly expanding energy consumption and power demand, the depletion of fossil-fuels-based energy resources, together with the collateral environmental pollution derived from their employment, are two critical challenges for human society [1]. In this scenario, renewable energy storage and conversion to green energy carriers have attracted tremendous interest. Electrocatalytic processes, often exploited in these research branches, have been widely considered one of the most promising technologies that can bring answers to both the energy and environmental crisis [2].

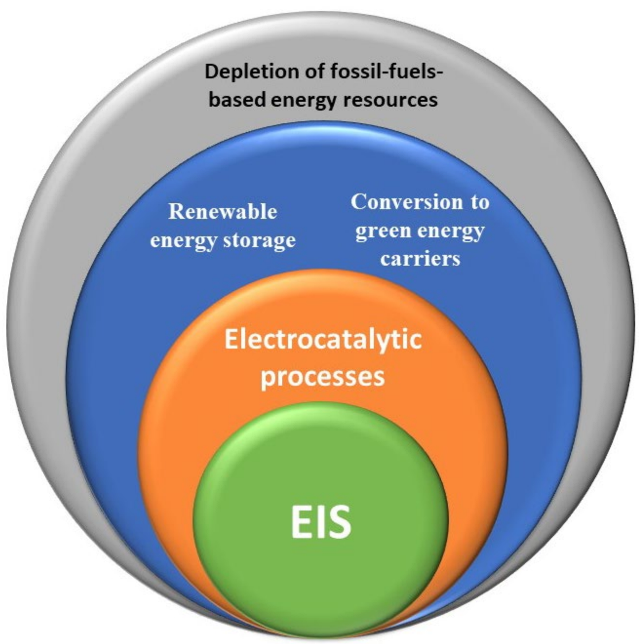


Figure 1: EIS position in green chemistry electrocatalysis landscape. EIS is nowadays a fundamental tool used to fully understand electrocatalytic processes, exploited in renewable energy storage and conversion to green energy carriers, studied to answer to depletion of fossil-fuels-based energy resources.

Electrocatalysis can be defined as a heterogeneous catalytic process happening on an electrode surface thanks to the introduction of an active material that facilitates the conversion between electrical and chemical energy. It provides new reaction pathways, which occur at the electrode-electrolyte interface, under the same potential or electric field without interfering with the electron transport rate. Therefore, the final goal of electrocatalysis is to increase the reaction rate or, in other words, the produced electrical current, via the decrease of activation energy of the target reaction [3]. Electrocatalytic reactions gained increasing interest in the past years, especially for energy conversion pathways, including oxidation processes such as oxygen evolution reaction (OER) [4] and methanol oxidation reaction (MOR) [5], as well as reduction processes like hydrogen evolution reaction (HER) [6], oxygen reduction reaction (ORR) [7], $CO_2$ reduction reaction ($CO_2$RR) [8], CO reduction reaction (CORR) [9] and, since very recently, nitrogen reduction reaction ($N_2$RR) [10]. Despite the intense research level, a deep understanding and demonstration of most of the electrocatalytic reaction mechanisms of the previously listed reactions are challenging, with still unknown pathways, which impedes a rational design and optimization of new electrocatalysts materials. The classical electrochemical techniques might not always be sufficient to determine electrode-electrolyte interface structure, the reaction intermediates, and the ultrafast reaction process involved, which is where electrochemical impedance spectroscopy (EIS) can play (Figure 1) a major role [11].

EIS is a versatile, well-established, and powerful tool for investigating the mechanisms of electrocatalytic reactions via the study of charge transfer and transport processes [12]. The impedance function of the studied system is generally analyzed by fitting it to an equivalent electrical circuit model (ECM) consisting of common electrical elements [13]. To be meaningful, the elements in the model should be a real representation of the physical electrochemical phenomena happening in the system [14].

Nowadays, EIS is omnipresent, often combined with cyclic voltammetry (CV), to characterize new electrocatalysts and electrochemical devices (see Figure 2). However, the last few years have witnessed an alternative and different use, that is, as a diagnostic tool. In fact, EIS is becoming a suitable technique to exploit during an electrochemical device's online operation. It can give insights into the actual working condition and, in some cases, into possible future device issues. This short review will cover the three main R&D fields where EIS technique has been exploited as a diagnostic tool, i.e., identifying the nature of an issue by examining the EIS spectra.

It is not a surprise that the fields of interest that will be discussed are those close to the market. In market-oriented applications, there is a need for quick and reliable answers to any issues happening in the electrochemical system, rather than a deep understanding of the involved chemistry. On the other hand, it could be unusual to see biosensors listed in the electrocatalytic-based application, but this will be clarified in its appropriate section.

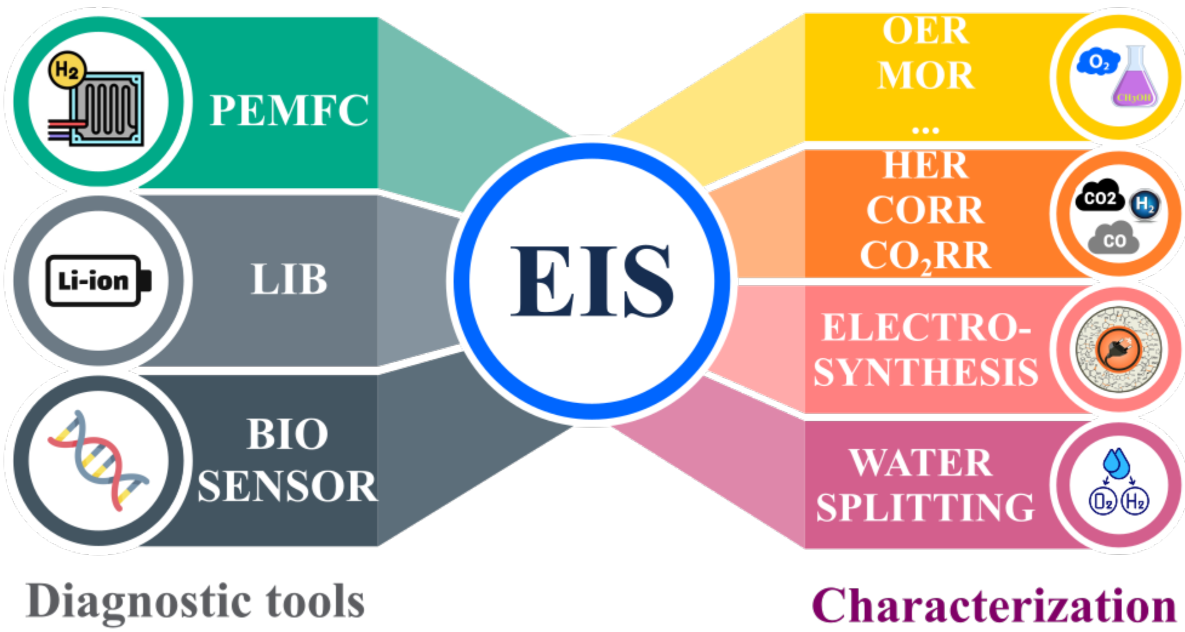


Figure 2. Schematic diagram of the most common EIS uses in electrocatalytic processes.

**EIS basis**

EIS principles and background have extensively been discussed in valuable books [15], reviews [13, 14], and tutorials [15, 16]; therefore, this section will rather provide the reader with a very brief description of the key concepts. Electrochemical impedance is usually measured by applying a small sinusoidal alternated current (AC, from less than 1 mHz to more than 1 MHz of frequency) to an electrochemical cell at a fixed applied potential and then measuring the resulting AC signal response through the cell. Through some mathematical transformations, it is possible to obtain an impedance value (expressed in terms of a magnitude, $Z_0$, and a phase shift, $\Phi$) of the cell per each frequency. The most common way to represent it is the so-called "Nyquist Plot", in which the real part ($Z_{real}$) is plotted on the X-axis and the imaginary part ($Z_{imag}$) is plotted on the Y-axis. The impedance function of the studied system is generally analyzed by fitting it to an equivalent electrical circuit model consisting of common electrical elements such as resistors, capacitors, inductances and other specific circuit elements [20].

Analyzing impedance evolution over frequency span makes it possible to obtain an in situ and simple diagnostics system that works under operative conditions. It is also possible to differentiate among the different components of the electrochemical cell, such as cathode, anode, membrane, electrolyte, etc.

Moreover, systematically varying process parameters (applied potential or current, temperature, pressure, presence of light, electrolyte concentration, etc.) or internal components (electrodes materials, kind of electrolyte, catalyst, membrane, etc.) and examining the resulting impedance trend, useful insight on how such variables affect the system can be acquired. In other words, once every dependency is known, monitoring the impedance at a carefully chosen frequency makes it possible to monitor the system status and, subsequently, implement corrective actions (e.g. by varying operation conditions) to maintain the cell performance.

**Lithium-Ion Batteries**

Among all electrocatalytic process applications, lithium-ion batteries (LIB) currently have a high impact on everyone's life. Accurate prediction of battery state of health (SoH), state of charge (SoC), and remaining useful life (RUL) is crucial to avoid unexpected capacity fade or to inform the user whether a battery should be replaced or not [21]. Such checks must be done in situ and periodically while batteries are running to understand the actual condition and forecast the remaining power. In this perspective, EIS became the key technique to evaluate the above-mentioned figures of merit [18, 19, 20, 25]. Due to their self-learning abilities, data-driven methods are the most recent and promising ways to analyze the multiple and complex information accompanied by EIS data. Zhang et al. [26] proposed to use neural networks to exploit EIS for the battery SOH estimation. In their work, they combined real-time EIS data with Gaussian process machine learning. By training the algorithm with thousands of EIS spectra of different batteries under different conditions, finally, the model was able to predict the SoH and the RUL with very good accuracy (Figure 3) from a single impedance measurement.

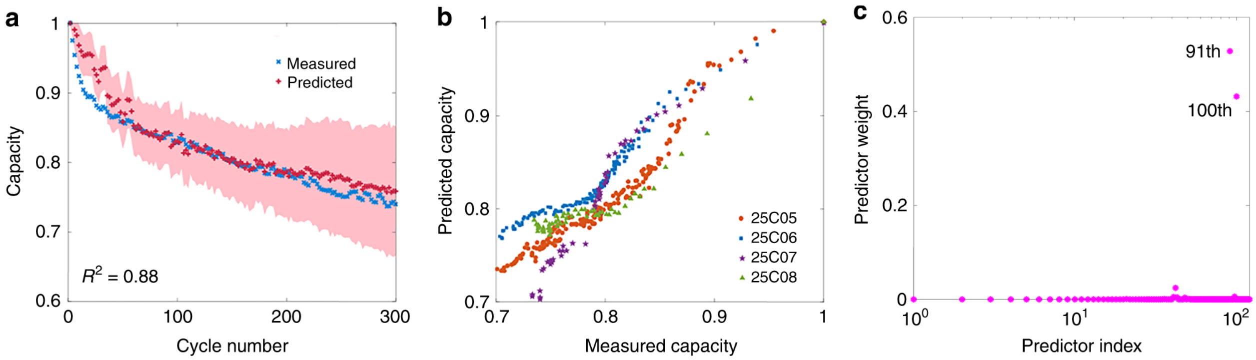


Figure 3. a) Estimated (red curve) and measured (blue curve) capacity as a function of cycle number for the 25C05 cell. The coefficient of determination ($R^2$) of this model is shown on the left bottom. b) The measured capacity against the estimated capacity of all four testing cells cycled at 25 °C. The capacity is normalized against the starting capacity in each case. c) ARD shows that the impedance at low frequency is most correlated with degradation. The pink points correspond to the 120 frequencies in the range of 0.02 Hz–20 kHz. The GPR model assigns the largest weights to the 91st and 100th features, corresponding to 17.80 and 2.16 Hz, respectively. The less relevant features have weights close to zero. Reproduced from [26].

Babaeiyazdi et al. [27] also used a machine learning (ML) approach in the form of a linear regression (LR) and a Gaussian process regression (GPR) algorithm. The two models were trained only with selected features of different datasets at various temperatures and different SoCs. The predictions over the test set indicated an error of less than 3.8% for the GPR model in the evaluation of the SoC.

Many other works are going towards machine learning due to the intrinsic characteristics of EIS spectra being too sensitive to the test conditions. This issue can be avoided by using a data-driven approach [7, 28].

**Fuel Cells**

If we consider LIBs the present, for sure, fuel cells (FCs), in their different declinations [30], are the future. They provide a clean, efficient, and probably the most flexible chemical-to-electrical energy conversion technology [31]. Figure 4 shows the most recurrent faulty conditions that lead to different irreversible consequences. It gives a clear view of the complexity of the many processes interacting in parallel in a proton exchange membrane (PEM) fuel cell.

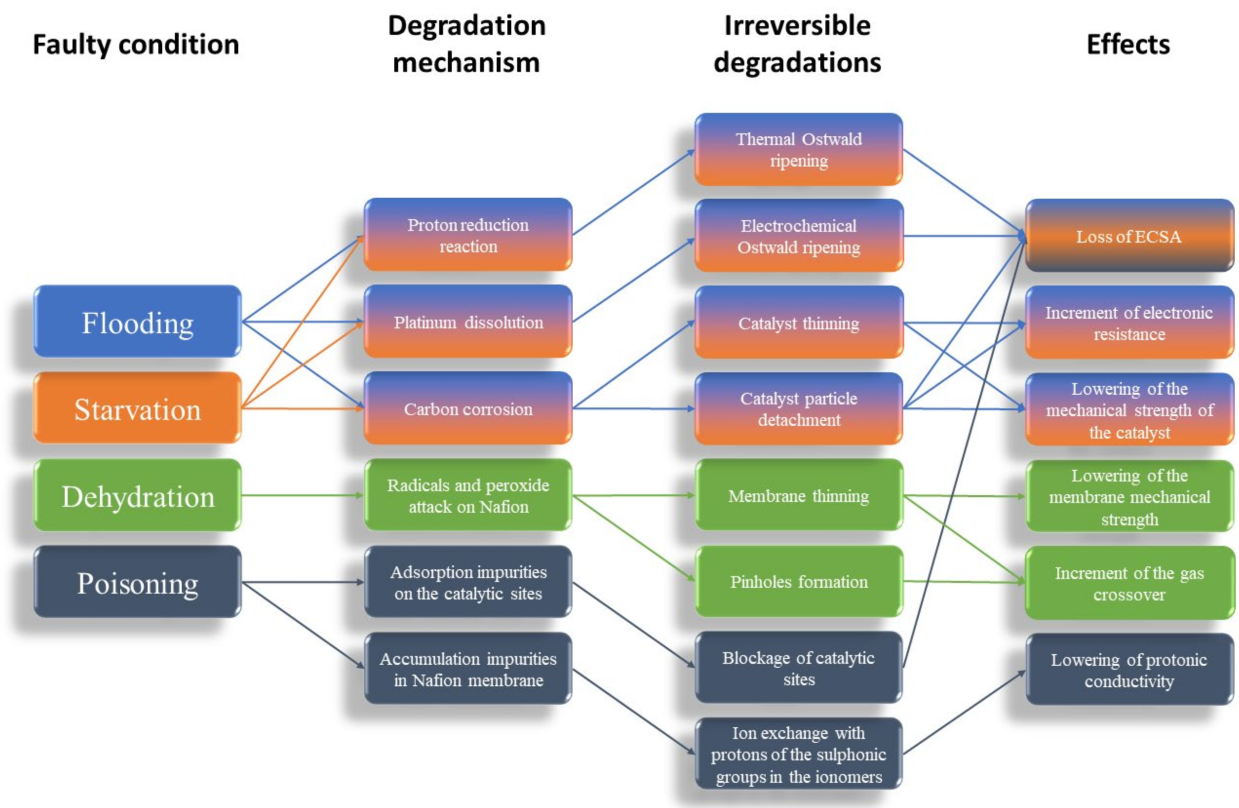


Figure 4. Schematic relations between faulty conditions, degradation mechanisms, irreversible degradation, and their effect. Reproduced from [32].

The possible source of problems and their related consequences are so variegated that, even in this case, EIS is very useful during their operational phase. In fact, EIS can differentiate the various contributions giving useful hints of where hides the issue [26, 27, 28]. Halvorsen et al. [35] implemented a new algorithm that indicates the state of aging of a PEMFC by checking the low-frequency intercept with the real axis of the Nyquist diagram in a fuel cell's impedance spectrum. Although it was only simulated and not yet tested in a real environment, the proposed solution is claimed to be effective and simple enough to be integrated into commercial devices for online monitoring.

On the other hand, Najafi et al. [36] focused their work on defining the best EIS frequency range for their fault recognition sequence. Yan et a. [37] made one step further in developing an active control strategy that integrates actions to recover from the detected faulty condition. Moreover, neural networks or, more in general, machine learning solutions that exploit EIS spectra have also been developed for PEMFCs to detect cells' conditions [32, 33, 34, 40].

**Biosensors**

A special category of electrocatalytic processes concerns the biosensors field [42]. In fact, electrocatalytic signal amplification has become an essential aid in biology [43]. The speed of electrons transfer on the electrodes can affect the biological transducer response time and accuracy. For this reason, different materials are used as a mediator to improve the response of the electrochemical sensor by their electrocatalytic effect and to facilitate electron transfer [44][45][46].

Among all the several detection techniques for biosensors, EIS is emerging for its already cited features [47][48][49][50]. Recently, Li and his co-workers [51] presented a paper-based EIS biosensor with improved sensitivity employing zinc oxide nanowires (ZnO NWs) and iron-based electron mediators [51]. The conceived system was able to detect a concentration of 0.4 pg $ml^{-1}$ p24 antigen as a marker for human immunodeficiency virus (HIV). The paper-based ZnO-NW-enhanced EIS biosensor was also preliminarily tested for CR3022 antibody specific to the spike glycoprotein S1 of SARS-CoV-2 in human serum as a marker for COVID-19, showing the ability to detect four different concentrations. With the same principle of exploiting the electrocatalytic properties of nickel nanowire, Wang et al. [52] could detect Salmonella bacteria with a limit of detection of 80 CFU/ml. Also, in this area, machine learning, in conjunction with EIS, plays a major role. In the work of Xu and co-workers [45], a machine learning system was trained to use EIS spectra to detect *E.coli. as* summarized in Figure 5. The ML model correctly predicted all the E.coli concentrations used in the training data set and detected the other two bacteria concentrations accurately, never used to train the algorithm, showing its adaptability and reliability to dataset variations.

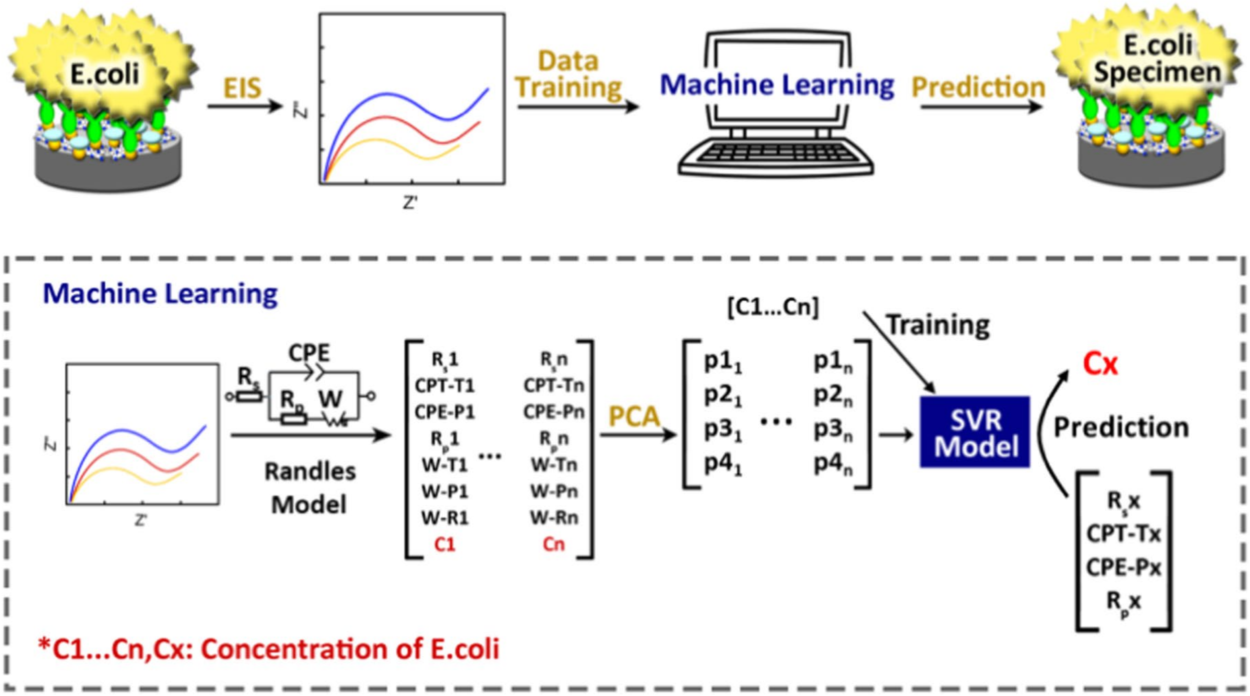


Figure 5. Schematic representation of the machine learning-based EIS biosensor system for *E.coli* detection. PCA: principle component analysis; SVR: supporting vector regression. Reproduced from [53].

**EIS data interpretation**

One of the obstacles to the massive use of EIS for online and real-time data analysis is the complexity of spectra analysis. A correct ECM requires an accurate knowledge of the different electrochemical processes contributing to the overall cell impedance. An alternative tool for analyzing EIS data emerging in the last few years is called distribution of relaxation times (DRT). DRT is a series of mathematical operations that allow finding the time constants of the said unknown electrochemical processes, from which it is possible to extract useful information that is not so discernible only by analyzing the EIS curve in the Nyquist plot [54, 55, 34]. Recently, several researchers are applying the DRT method to diagnostic categories shown in Figure 2 to track their changes and to understand how the behavior of the specific device evolves [56][57][58].

**Conclusion and future perspective**

The development of EIS over the past few decades has enabled a better understanding of most electrochemical systems operating in our modern devices. The flexibility of EIS and its potentiality to fetch in situ and online quantitative information from complicated electrochemical systems made it a crucial and complementary tool for electrochemists. Nonetheless, rigorous considerations of the choice of experimental conditions and pertinent mathematical models are necessary to accurately describe the physics phenomena and reaction mechanisms involved in the system. EIS is now used as a standard tool for electrochemical characterization, but it is emerging as a diagnostic technique in the latest years.

Building a fully automated and trusted diagnostic tool exploiting EIS is still challenging. Spectra taken on a broad frequency range give much useful information, but the analysis and interpretation of such a large quantity of data are often troublesome. First, circuit model fittings hinder or oversimplify the underlying physics and chemistry of electrocatalytic processes. Secondly, many electrocatalytic systems are still not properly understood, although many research works are already available in the literature.

The good news is that it is not necessary to fully understand all the underlying processes for many monitoring tasks, but it is enough to locate, with a fair approximation degree, to act as quickly as possible. This is especially true for electrochemical cells used for commercial products (electric vehicles, power generators, sensing devices, etc.).

EIS data interpretation will progress in two major directions. The first is the rapid automated interpretation of data, mostly for a qualitative assessment. This path is predominated by a data-driven approach such as neural networks [59], support vector regression [60], and fuzzy systems [61]. An automated evaluation will enable the use of EIS spectra for different electrochemical cells used in commercial products such as SoH of electric vehicle batteries or more reliable responses from biosensors. The second contemplates EIS analysis as a component of a wider toolbox used by electrochemists to extensively understand all reaction mechanisms in specific electrochemical cells for electrosynthesis processes that are still in an R&D phase and at a low Technology Readiness Level (TRL 3-5), such as MOR, OER, HER, ORR, $CO_2$RR, CORR, $N_2$RR [54, 55]. However, in the future, EIS-based diagnosis tools will also be developed as a strategy to monitor and maintain the stability, catalytic performance, and selectivity of those novel electrocatalytic systems. Indeed, these technologies are envisaged to substitute fossil-fuel-based approaches for producing valuable chemicals and fuels from renewable resources and wastes in a circular economy approach. It is not a case that LIBs, PEMFCs, and Biosensors have a strong industrial dimension of the different applications in common. This will be, in our opinion, the leading characteristics that will consolidate the use of EIS to an alternative use other than as a characterization technique.

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