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Original

Diagnostics of electrocatalytic systems by electrochemical impedance spectroscopy / Sanginario, Alessandro; Hernández, Simelys. - In: CURRENT OPINION IN GREEN AND SUSTAINABLE CHEMISTRY. - ISSN 2452-2236. - ELETTRONICO. - 39:(2023). [10.1016/j.cogsc.2022.100727]

Availability:

This version is available at: 11583/2991700 since: 2024-10-08T09:27:51Z

Publisher:

Elsevier

Published

DOI:10.1016/j.cogsc.2022.100727

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<http://dx.doi.org/10.1016/j.cogsc.2022.100727>

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In situ diagnostics of electrocatalytic systems by electrochemical impedance spectroscopy

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1 Abstract

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

8 This review will focus on the use of the EIS technique as a diagnostic tool in the electrocatalysis field. Surprisingly,
9 among the numerous electrochemical reactions, the areas in which EIS is employed as a monitoring tool are very few.

10 The most important are the ones with a high technological maturity level and, therefore, that are already employed in
11 the industry or for commercial applications: e.g., batteries, fuel cells and biosensors. Devices belonging to these groups
12 need to control their working conditions with fast and reliable methods, even at the cost of losing a small amount of
13 precision degree. In this perspective, EIS is often used in combination with machine learning algorithms to develop
14 easy-to-use diagnostic devices that aim to a rapid indication of the system status rather than a precise understanding
15 of all the underlying processes.

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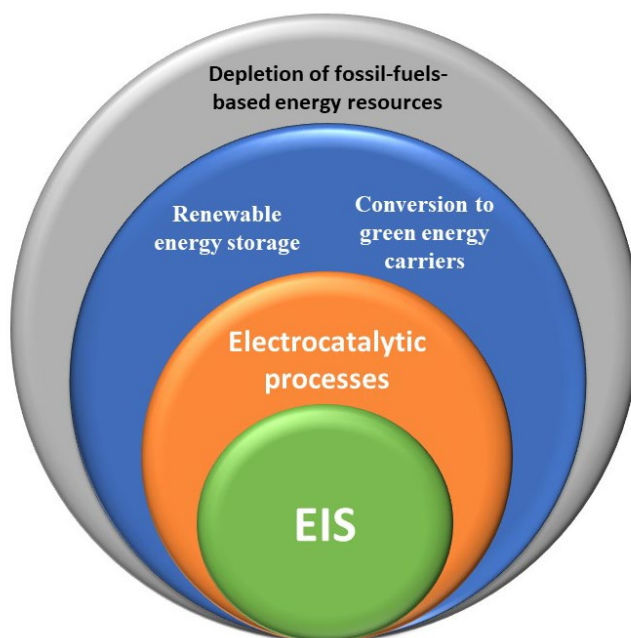
17 **Keywords**

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

19

20 **Introduction**

21 With quickly expanding energy consumption and power demand, the depletion of fossil-fuels-based energy resources,
22 together with the collateral environmental pollution derived from their employment, are two critical challenges for
23 human society [1]. In this scenario, renewable energy storage and conversion to green energy carriers have attracted
24 tremendous interest. Electrocatalytic processes, often exploited in these research branches, have been widely
25 considered one of the most promising technologies that can bring answers to both the energy and environmental crisis
26 [2].



27

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

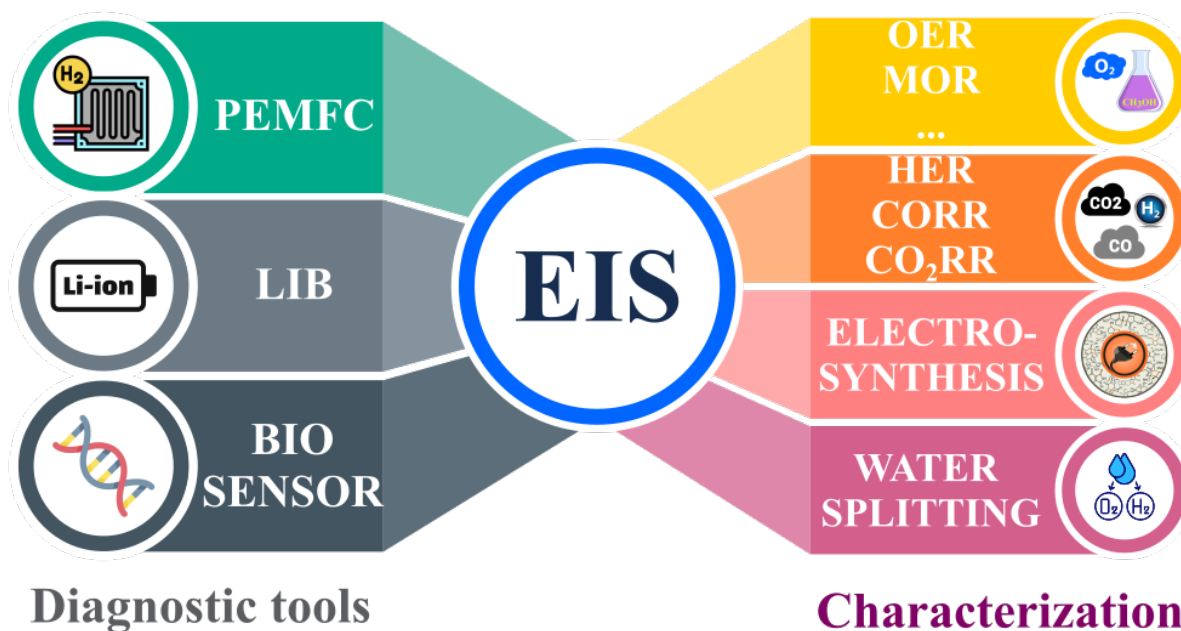
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32 Electrocatalysis can be defined as a heterogeneous catalytic process happening on an electrode surface thanks to the
33 introduction of an active material that facilitates the conversion between electrical and chemical energy. It provides
34 new reaction pathways, which occur at the electrode-electrolyte interface, under the same potential or electric field
35 without interfering with the electron transport rate. Therefore, the final goal of electrocatalysis is to increase the
36 reaction rate or, in other words, the produced electrical current, via the decrease of activation energy of the target
37 reaction [3]. Electrocatalytic reactions gained increasing interest in the past years, especially for energy conversion
38 pathways, including oxidation processes such as oxygen evolution reaction (OER) [4] and methanol oxidation reaction
39 (MOR) [5], as well as reduction processes like hydrogen evolution reaction (HER) [6], oxygen reduction reaction
40 (ORR) [7], CO₂ reduction reaction (CO₂RR) [8], CO reduction reaction (CORR) [9] and, since very recently, nitrogen
41 reduction reaction (N₂RR) [10]. Despite the intense research level, a deep understanding and demonstration of most
42 of the electrocatalytic reaction mechanisms of the previously listed reactions are challenging, with still unknown
43 pathways, which impedes a rational design and optimization of new electrocatalysts materials. The classical
44 electrochemical techniques might not always be sufficient to determine electrode-electrolyte interface structure, the
45 reaction intermediates, and the ultrafast reaction process involved, which is where electrochemical impedance
46 spectroscopy (EIS) can play (Figure 1) a major role [11].

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

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

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



62

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

64

65 **EIS basis**

66 EIS principles and background have extensively been discussed in valuable books [15], reviews [13, 14], and tutorials
 67 [15, 16]; therefore, this section will rather provide the reader with a very brief description of the key concepts.
 68 Electrochemical impedance is usually measured by applying a small sinusoidal alternated current (AC, from less than
 69 1 mHz to more than 1 MHz of frequency) to an electrochemical cell at a fixed applied potential and then measuring
 70 the resulting AC signal response through the cell. Through some mathematical transformations, it is possible to obtain
 71 an impedance value (expressed in terms of a magnitude, Z_0 , and a phase shift, Φ) of the cell per each frequency. The
 72 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
 73 and the imaginary part (Z_{imag}) is plotted on the Y-axis. The impedance function of the studied system is generally

74 analyzed by fitting it to an equivalent electrical circuit model consisting of common electrical elements such as
75 resistors, capacitors, inductances and other specific circuit elements [20].

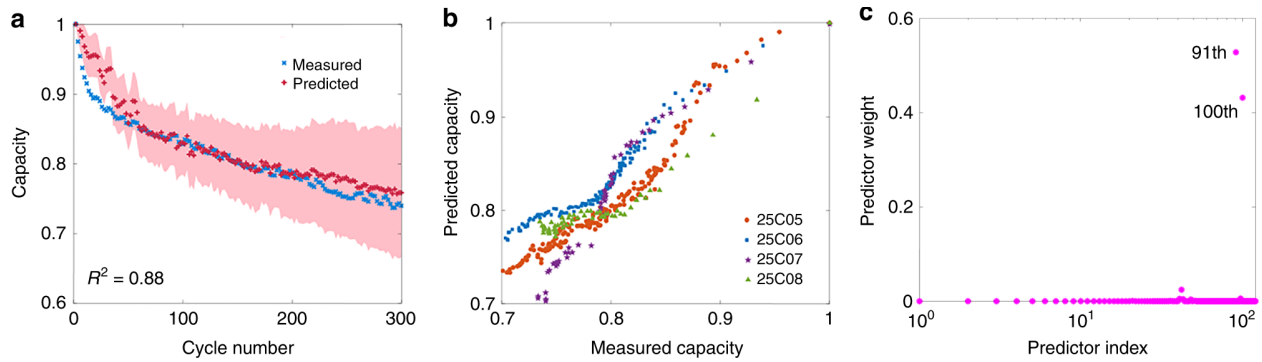
76 Analyzing impedance evolution over frequency span makes it possible to obtain an in situ and simple diagnostics
77 system that works under operative conditions. It is also possible to differentiate among the different components of
78 the electrochemical cell, such as cathode, anode, membrane, electrolyte,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

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

85

86 **Lithium-Ion Batteries**

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



98

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

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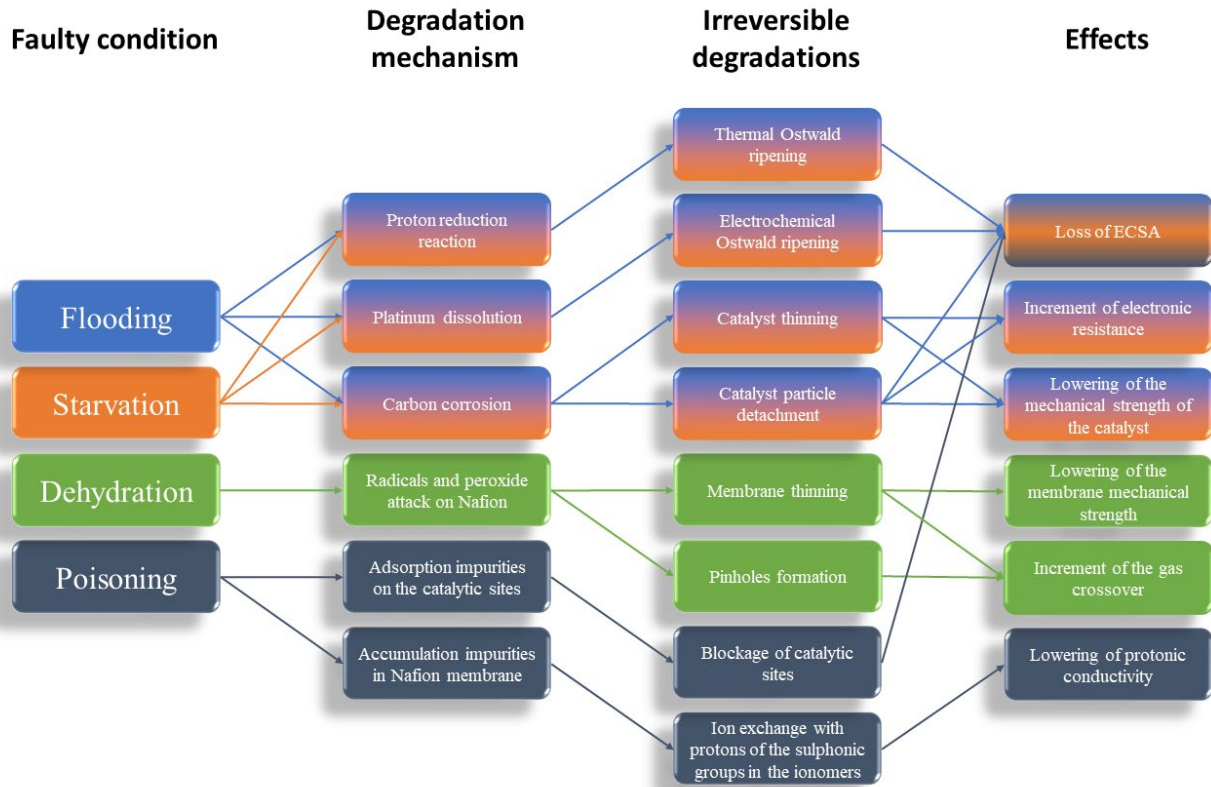
106 Babaeiyazdi et al. [27] also used a machine learning (ML) approach in the form of a linear regression (LR) and a
 107 Gaussian process regression (GPR) algorithm. The two models were trained only with selected features of different
 108 datasets at various temperatures and different SoCs. The predictions over the test set indicated an error of less than
 109 3.8% for the GPR model in the evaluation of the SoC.

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

112 Fuel Cells

113 If we consider LIBs the present, for sure, fuel cells (FCs), in their different declinations [30], are the future. They
 114 provide a clean, efficient, and probably the most flexible chemical-to-electrical energy conversion technology [31].

115 Figure 4 shows the most recurrent faulty conditions that lead to different irreversible consequences. It gives a clear
 116 view of the complexity of the many processes interacting in parallel in a proton exchange membrane (PEM) fuel cell.



117

118 Figure 4. Schematic relations between faulty conditions, degradation mechanisms, irreversible degradation, and their effect.

119

Reproduced from [32].

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

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

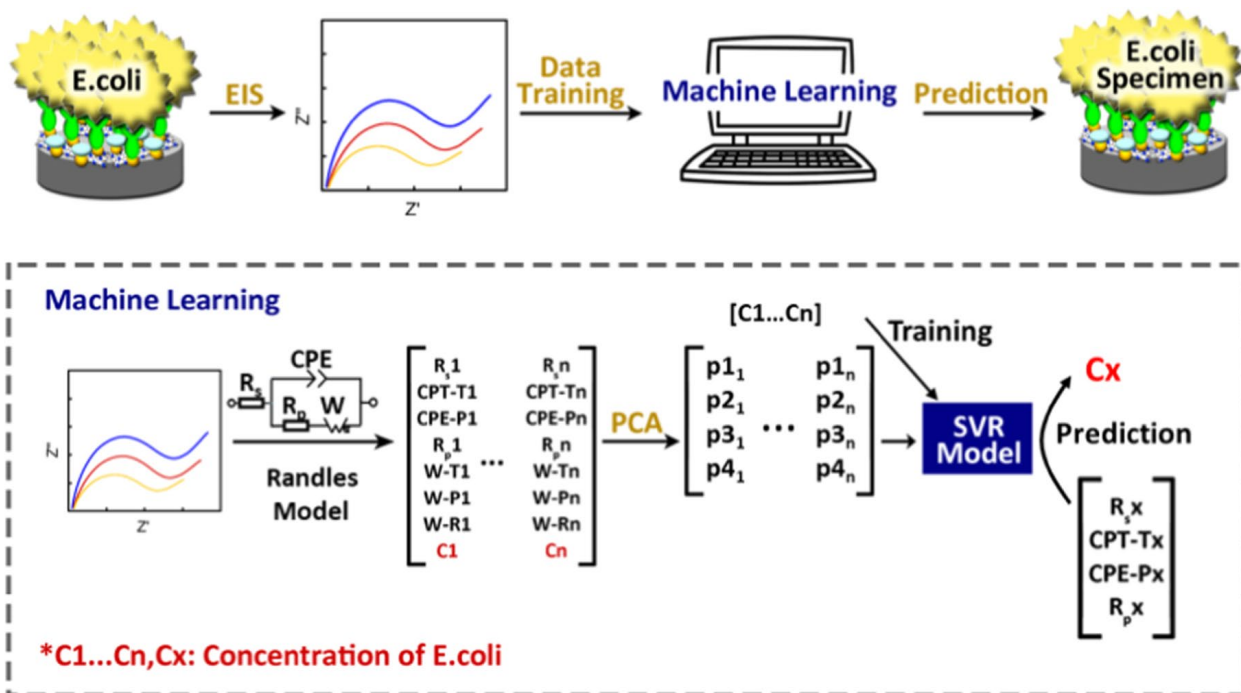
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131 **Biosensors**

132 A special category of electrocatalytic processes concerns the biosensors field [42]. In fact, electrocatalytic signal
133 amplification has become an essential aid in biology [43]. The speed of electrons transfer on the electrodes can affect
134 the biological transducer response time and accuracy. For this reason, different materials are used as a mediator to
135 improve the response of the electrochemical sensor by their electrocatalytic effect and to facilitate electron transfer
136 [44][45][46].

137 Among all the several detection techniques for biosensors, EIS is emerging for its already cited features
138 [47][48][49][50]. Recently, Li and his co-workers [51] presented a paper-based EIS biosensor with improved
139 sensitivity employing zinc oxide nanowires (ZnO NWs) and iron-based electron mediators [51]. The conceived system
140 was able to detect a concentration of 0.4 pg ml^{-1} p24 antigen as a marker for human immunodeficiency virus (HIV).
141 The paper-based ZnO-NW-enhanced EIS biosensor was also preliminarily tested for CR3022 antibody specific to the
142 spike glycoprotein S1 of SARS-CoV-2 in human serum as a marker for COVID-19, showing the ability to detect four
143 different concentrations. With the same principle of exploiting the electrocatalytic properties of nickel nanowire,
144 Wang et al. [52] could detect Salmonella bacteria with a limit of detection of 80 CFU/ml. Also, in this area, machine
145 learning, in conjunction with EIS, plays a major role. In the work of Xu and co-workers [45], a machine learning
146 system was trained to use EIS spectra to detect *E.coli. as* summarized in Figure 5. The ML model correctly predicted
147 all the E.coli concentrations used in the training data set and detected the other two bacteria concentrations accurately,
148 never used to train the algorithm, showing its adaptability and reliability to dataset variations.

149



150

151 Figure 5. Schematic representation of the machine learning-based EIS biosensor system for *E.coli* detection. PCA: principle

152 component analysis; SVR: supporting vector regression. Reproduced from [53].

153

154 **EIS data interpretation**

155 One of the obstacles to the massive use of EIS for online and real-time data analysis is the complexity of spectra

156 analysis. A correct ECM requires an accurate knowledge of the different electrochemical processes contributing to

157 the overall cell impedance. An alternative tool for analyzing EIS data emerging in the last few years is called

158 distribution of relaxation times (DRT). DRT is a series of mathematical operations that allow finding the time

159 constants of the said unknown electrochemical processes, from which it is possible to extract useful information that

160 is not so discernible only by analyzing the EIS curve in the Nyquist plot [54, 55, 34]. Recently, several researchers

161 are applying the DRT method to diagnostic categories shown in Figure 2 to track their changes and to understand how

162 the behavior of the specific device evolves [56][57][58].

163

164

165 **Conclusion and future perspective**

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

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

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

181 EIS data interpretation will progress in two major directions. The first is the rapid automated interpretation of data,
182 mostly for a qualitative assessment. This path is predominated by a data-driven approach such as neural networks
183 [59], support vector regression [60], and fuzzy systems [61]. An automated evaluation will enable the use of EIS
184 spectra for different electrochemical cells used in commercial products such as SoH of electric vehicle batteries or
185 more reliable responses from biosensors. The second contemplates EIS analysis as a component of a wider toolbox
186 used by electrochemists to extensively understand all reaction mechanisms in specific electrochemical cells for
187 electrosynthesis processes that are still in an R&D phase and at a low Technology Readiness Level (TRL 3-5), such
188 as MOR, OER, HER, ORR, CO₂RR, CORR, N₂RR [54, 55]. However, in the future, EIS-based diagnosis tools will
189 also be developed as a strategy to monitor and maintain the stability, catalytic performance, and selectivity of those
190 novel electrocatalytic systems. Indeed, these technologies are envisaged to substitute fossil-fuel-based approaches for

191 producing valuable chemicals and fuels from renewable resources and wastes in a circular economy approach. It is
192 not a case that LIBs, PEMFCs, and Biosensors have a strong industrial dimension of the different applications in
193 common. This will be, in our opinion, the leading characteristics that will consolidate the use of EIS to an alternative
194 use other than as a characterization technique.

195

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