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Trends in electrochemical impedance spectroscopy involving nanocomposite transducers: Characterization, architecture surface and bio-sensing

Jose Muñoz [a, **], Raquel Montes [b], Mireia Baeza [c, *]

[a] Molecular Nanoscience and Organic Materials Group, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), 08193 Bellaterra (Cerdanyola del Vallès), Barcelona, Spain
[b] GENOCOV Research Group, Department of Chemical, Biological and Environmental Engineering, School of Engineering, Universitat Autònoma de Barcelona, Carrer de les Sitges, 08193 Bellaterra (Cerdanyola del Vallès), Barcelona, Spain
[c] Department of Chemistry, Faculty of Science, Edifici C-Nord, Universitat Autònoma de Barcelona, Carrer del Til·lers, 08193 Bellaterra (Cerdanyola del Vallès), Barcelona, Spain

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ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) has gained widespread application for the characterization of functionalized electrode surfaces and for the transduction of bio-sensing events. However, bio-sensors using EIS detection have to be carefully designed to minimize non-specific binding of the analyte. In this sense, surface engineering by using nanocomposite materials (NCs) is advantageous due to the increased electrode surface area, improved electrical conductivity of the sensing interface, chemical accessibility to the analyte and electroanalysis. Accordingly, this review summarizes the basis of the EIS technique as well as its implementation not only in common Faradaic EIS *(impedimetric)* bio-sensors using NCs as highly sensitive transducer platforms but also in not so conventional non-Faradaic EIS *(capacitive)* approaches. Finally, it is also highlighted the feasibility of EIS as an alternative characterization tool towards the optimization of NC electrodes in terms of loading ratios for electroanalytical improvements, summarizing the latest promising results in nanocomposite carbon paste electrodes.

1. Introduction

Electrochemical Impedance Spectroscopy (EIS) is a powerful method of analyzing the complex electrical resistance of a system and is sensitive to surface phenomena and changes of bulk properties. The term *impedance* was coined in 1886 by the electrical engineer, mathematician and physicist Oliver Heaviside, who adapted complex numbers to the study of electrical circuits [1]. The method of impedance measurements is widely used in many fields of electrochemistry, such as electrode kinetics, double layers studies, batteries, corrosion, solid-state electrochemistry and bio-sensing [2–4].

EIS technique has become a popular electrochemical tool for the detection of a wide range of chemical and biological targets in terms of electrochemical change of electrode interfaces, as it is revealed by the rapidly number increased of bio-sensors based on impedimetric measurements in the last years [5–7]. The use of EIS transducer signal in biological sensorial applications is mainly based on the interactions between the biological receptor and the target species selectively adsorbed from the solution. Such interactions cause a change on interfacial electron transfer kinetics between a redox probe in solution and the conducting electrode sites. This electrochemical change is then detectable by monitoring the charge-transfer resistance (R_{ct}) that commonly increase in the same proportion given the increase in the quantity of targets bound to the receptive surface [8,9]. However, while the selectivity of a bio-sensor mostly relies on the specificity of the molecular recognition element, several analytical parameters, such as sensitivity, response time and limit of detection, strongly depend on the physicochemical properties of the transducer, which can be improved by the utilization of proper materials and/or the design of new architecture surfaces.

In this sense, functional nanomaterials, and especially nanocomposite (NC) materials, play a critical role in signal transduction

* Corresponding author.
** Corresponding author.
E-mail addresses: jmunoz@icmab.es (J. Muñoz), mariadelmar.baeza@uab.cat (M. Baeza).

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since such nanosized compounds are shown to clearly increase the analytical performance [10–13], providing not only a synergetic effect among catalytic activity, conductivity, and biocompatibility to accelerate the signal transduction but also amplify bio-recognition events with specifically designed signal tags. These improvements are mainly related to an increased surface area that enhances accessibility for the analyte to the receptor unit; this fact leads to the achievement of highly sensitive bio-sensing platforms [14–16]. In general, a NC material can be defined as the result of combining two or more different materials where, at least, one of the constituent parts has a nanometer scale dimension [17], keeping their individual identities but still impart their properties to the product resulting from their combination. Thus, building blocks with dimensions in the nanosize range enable us the possibility to design and develop new NCs with unprecedented versatility and improvement in their physical, chemical and electrochemical properties, being also able to act as transducers for the signal capture. Among the vast amount of examples where nanomaterials demonstrate their superiority to bulk materials, the development of NC materials based on a conductive phase as carbon nanoallotropes (e.g., carbon nanotubes, graphene and related) dispersed in an insulating polymeric matrix (such as epoxy, methacrylate, Teflon, etc.), has led to important advances in the analytical electrochemistry field, especially in the development of sensors and biosensors devices [18–20].

The strong demand to generate devices that respond selectively to specific bio-molecules opens up alternative strategies associated with designing either Faradaic or non-Faradaic bio-interfaces, due to each approach needs specific surface architecture according to either resistive or capacitive transducer signal, respectively [21–23]. Regarding that, self-assembled monolayers (SAMs) have found widespread utility in the fabrication of electrochemical biosensors [24,25], owing to the mainstream development of gold-thiol SAMs in the early 1980s [26]. In contrast to traditional Faradaic EIS (*impedimetric*) methods where the determination of R_{ct} require the addition of a redox probe to the analytical solution prior to analysis and a subsequent fitting of data to an equivalent circuit, non-Faradaic (*capacitive*) methods provide an alternative strategy where no redox element is added to solution, being amenable to miniaturization [27,28]. The signal of non-Faradaic EIS transducers is mainly due to capacitance changes on the electrode–electrolyte interface that can be easily monitored by double-layer capacitance (C_{dl}) means. Further, non-Faradaic technique can not only be applied in traditional analysis of dielectric films [29,30], but also can be combined with surfaced tethered redox reporters in establishing highly sensitive label free assay based on Electrochemical Capacitance Spectroscopy (ECS), which measures "capacitive charging" (redox capacitance) [27,31].

Recently, EIS technique has also been exploited as promising characterization tool towards the optimization of NC-based electrodes by means of composition ratios; especially in the nano(bio) composite carbon paste electrodes field [32,33]. Briefly, both the nature of the raw carbon filler and its loading throughout the insulating polymeric matrix directly affects the rate of electron transfer, the material stability and the background capacitance current [34,35]. Therefore, an accurate loading characterization of each component is crucial in order to achieve high signal-to-noise ratios which ensure significant reproducibility, optimal sensitivity, fast response time as well as low detection limits.

Accordingly, the framework of the current review tends to offer a comprehensive summary of the last trends in EIS approaches where NC materials are involved as highly sensitive transducer platforms, fact that might serve as a general outlook for planning further research. For this aim, this review overviews *(i)* the basis of the EIS technique; *(ii)* the latest development of EIS bio-sensors, which usually focus upon certain bio-recognition events in conjunction with NC-based electrodes; *(iii)* the demands and strategies associated with surface engineering for either Faradaic (*impedimetric*) or non-Faradaic (*capacitive*) EIS transducer development, highlighting those platforms based on SAMs; and *(iv)* the use of EIS technique as an alternative characterization tool for NC electrodes optimization (especially for NC-CPEs), fact that allows for an improvement on their electrochemical and electroanalytical performances.

2. General principles

EIS technique provides electric information in the frequency domain. With this technique, a process occurring in an electrochemical cell can be modeled to equivalent circuits derived from using combination of resistors (R), capacitors (C) and/or inductors (L). Interpretation of EIS measurements is usually done by fitting the impedance data to an equivalent electrical circuit that is representative of the physical processes taking place in the system under investigation. By using equivalent circuits, the experimental spectrum can be fitted with the theoretical curve corresponding to the suitable circuit model, thus obtaining the values of electrical parameters [36–39].

Impedance is defined as the ability of a circuit element to resist the flow of current and therefore, is simply the opposition force to electrical current in a circuit, which is measured in the same units as resistance (Ω). EIS generally measures the resulting of applying a sinusoidal alternating current (AC) potential to an electrochemical cell and measuring the AC current that crosses through the cell. When an oscillating potential is applied to an electrode surface, the resulting current has the same frequency as the applied potential but may be shifted in phase. This phase-shift is dependent on the relative resistive and capacitive features of the electrochemical system. Consequently, the phase-shift can be used to monitor physical processes at the electrode surface. As it is shown in Fig. 1A, a sinusoidal AC voltage, E(t), of a small magnitude, E^o, is applied to an electrode over a range of frequencies (ω), and the resulting sinusoidal current is measured. The resulting AC current, I(t), is of the same frequency as the applied potential, but shifted in phase. The phase-shift is reported as the phase angle (θ) as it relates to the period of the sinusoidal waves.

This phase angle (or phase-shift) represents the relative capacitive, resistive and inductive character of the electrochemical system. Equations (1) and (2) describe the applied potential E(t) and resulting current I(t), respectively, where t is time and I^o is the magnitude of the current oscillations [3,40].

$$E(t) = E^o \sin(\omega t) \tag{1}$$

$$I(t) = I^o \sin(\omega t - \theta) \tag{2}$$

The impedance of the system (Z) can be calculated by means of an expression analogous to Ohm's Law, Equation (3):

$$Z = \frac{E(t)}{I(t)} \tag{3}$$

Using the Euler's formula (Equation (4)), and taking into account that the impedance has an amplitude $Z^o = E^o/I^o$ and a phase-shift φ, it is possible to express Z in terms of complex numbers, following Equation (5), where Z_{real} is the real part, $j = \sqrt{-1}$ and Z_{imag} is the imaginary part of the impedance.

$$e^{j\varphi} = \cos(\varphi) + j \sin(\varphi) \tag{4}$$