Mini Review

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Faradaic and non-faradaic electrochemical impedance spectroscopy as transduction techniques for sensing applications

Abstract

Electrochemical Impedance Spectroscopy (EIS) stands out as a powerful technique for application in electroanalytical devices. Especially due to the possibility of label-free performance, use of miniaturized systems, in situ measurements and the relative low cost, impedimetric sensors have attracted particular attention in the recognition of analytes of medical, environmental and industrial interests. Depending on the presence or absence of redox species in the electrode or in the electrolyte, the technique can be categorized as faradaic or non-faradaic EIS respectively. The choice of the most suitable sensing method relies mainly on the expected application. Despite the non-faradaic methods presents the advantages of the application in point-of-care devices due to the possibility of miniaturization of the electrodes and the absence of redox couple, the faradaic sensors tends to be more sensitive.

Keywords: electrochemical impedance spectroscopy, sensor, faradaic EIS, non-faradaic EIS

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Introduction

Electrochemical techniques have been widely employed to detect and/or quantify molecules of medical, environmental and industrial interests. Among traditional techniques such as potentiometry, amperometry and conductometry, the Electrochemical Impedance Spectroscopy (EIS) has gained great attention as an analytical tool for a broad range of analytes, mainly because it can be performed as a non-destructive method and it enables *in situ* measurements.[1,2] Moreover, EIS exempt the use of special reagents, which makes it suitable for label-free applications, which significantly diminishes its cost in relation to other techniques and makes it easier to perform.[3] In common, all the electrochemical sensors consist on relating a measurable output electrical signal to the changes in the structure (usually the surface) of an electrode because of the recognition of a target analyte. The in-depth understanding of the mechanisms and fundaments involving the sensing phenomena is a challenge in electroanalytical techniques and can lead to the improvement of the main desirable characteristics of a sensor: the selectivity, stability and sensibility.[4] In this sense, this minireview presents the main aspects regarding the EIS as a technique for application in sensors based on its two categories of performance: the Faradaic and non-faradaic EIS.

EIS theory

The EIS basis lies on the development of multiple microscopic processes when an electrode/electrolyte system suffers from an electrical stimulus. This small perturbation can provoke the transfer of electrons in electronic conductors and the transport of charged species from the electrode to the electrolyte (and *vice-versa*) due to the occurrence of oxidation and reduction reactions. Accordingly, the resultant flow rate of electrons and charges is a function of the resistance of both electrode and electrolyte as well as it depends on the

reaction rates that take place on the interface.[5] Basically, a sinusoidal AC potential (potenciostatic EIS) or current (galvanostatic EIS) is applied to an electrochemical system under study and the resultant AC current ou potential is measured as a frequency-dependent parameter. The ratio between the applied potential $E(\omega,t)$, which can also be superimposed by a constant DC potential, and the current $I(\omega,t)$ is the impedance $Z(\omega,t)$. Herein, ω is the angular frequency ($\omega=2\pi f$, where f is the variable frequency), t is the time, $|Z|$ is the magnitude of impedance, Z' is the real impedance, Z'' is the imaginary impedance, in which j is the imaginary number $\sqrt{-1}$, and φ is the angle phase between the potential and current signals.[6]

$$Z(\omega,t) = \frac{E(\omega,t)}{I(\omega,t)} = \left|Z(\omega,t)\right| e^{j\varphi} = \left|Z(\omega,t)\right|(\cos\varphi + j\sin\varphi)$$

$$Z(\omega,t) = Z'(\omega) + jZ''(\omega)$$

Typically, impedance data is represented as a function of Z' and Z'' (Nyquist diagram) or as a function of the frequency, $|Z|$ and/or φ (Bode diagram). By exploiting these graphical representations in certain frequency ranges, it is possible to assess some interfacial characteristics of an electrode as well as the conductive features of the electrolyte. However, due to the complex composition of the global impedance from an electrochemical cell, the EIS data is commonly modeled to an electrical equivalent circuit in order to further analyze the inductive, capacitive and resistive components.[8] EIS comprises two groups: the faradaic and non-Faradaic EIS. The use of one or the other terminology is associated to the occurrence of electrical charge transfer across an interface due to the presence or absence of redox species.[3] Based mainly on the characteristics of the transducer substrate, the electrolyte and the application of interest, one can elect the most appropriate technique to develop an electrochemical sensor.

Faradaic sensors

In faradaic EIS, reduction and/or oxidation reactions among electroactive species take place at the electrode leading to the generation of an electrical current[3] Thus, the faradaic sensors require the presence of redox probes and the application of DC conditions to promote the development of the electrochemical reactions. This type of EIS receives this name because the generated current obeys the Ohm's Law, which means that the faradaic current is related to the number of electrons transferred in the redox reactions (n), to the Faraday constant (F), the surface area of the electrode (A) and the flux of electroactive molecules at the interface boundary (j). [9]

$$I = nFAj$$

By means of the current generated from the redox reactions, the faradaic sensors can achieve higher sensitivity in comparison to the non-faradaic devices.[10] To model the appropriate equivalent circuit associated to faradaic sensors, besides the electrolyte resistance and the capacitance (that is usually replaced by a constant phase element – CPE), it must take in account the effect of a charge transfer resistance (R_{ct}) and a Warburg impedance (Z_w). The R_{ct} is a consequence of the potential generated by the oxidative and reductive phenomena at the electrode as well as of the repulsion or stearic effect caused by the charged species that arrives to the conductive surface.[3] Accordingly, the Z_w results from the diffusion of the electroactive species from the bulk solution to the electrode. Graphically, R_{ct} can be determined by the diameter of a semicircle in the Nyquist plot and Z_w can be deducted from a 45° inclined straight line at low frequencies[11] Despite the reduction and oxidation reactions are often associated to the presence of a redox couple in the electrolyte ($Fe(CN)_6^{3-/4-}$ is commonly employed as a redox pair in the literature), the redox phenomena can also occur in the structure of the electrode. For example, some conductive polymers such as polyaniline, polypyrrole and polythiophene possess the ability of conduct charge along their chain due to doping mechanisms.[12]

Non-faradaic sensors

Contrary to the faradaic EIS, the non-faradaic method does not demand the use of redox couples and, consequently, no reference electrode is necessary, because no DC potential is required[10] These features make this kind of sensors more amenable to miniaturization and to online/real-time applications. In this kind of technique, by charging and discharging the double-layer capacitance, it is possible to assess the dielectric changes on the electrode. Thus, the impedance of a non-faradaic sensor arises from the effect caused by the insulating characteristics of the target analyte bond to the conductive substrate.[13] Typically, the most valuable impedance parameter in this case is the double layer capacitance and it is only limited by the nature of the charge carriers and their concentration in the boundary layer of the transducer substrate.[3] Nonetheless, the |Z| and ϕ components are adequate transducer parameters.[14] In this case, the equivalent circuit consists of a combination of resistors and capacitors. The double layer capacitance (C) is described by the Helmholtz model as a function of the free space permittivity (ε_0), the relative solution permittivity (ε_r), the distance (d) of the Helmholtz layer and the surface area of the electrode (A)[15]

$$C = \frac{\varepsilon_0 \varepsilon_r}{d} A$$

Conclusion

Both faradaic and non-faradaic EIS present relevant advantages as transducer techniques in electrochemical sensors for various applications. In the faradaic mode, the charge transfer resistance is the impedance component correlated to the concentration of an analyte of interest and it is a result of the current generated from the reduction and oxidation reactions among electroactive species. On the other hand, the capacitance is generally the most important transducer term to interpret the recognition of a certain analyte in non-faradaic EIS. Despite less sensitive, the non-Faradaic sensor is a promising candidate for real-time applications because it does not require the presence of redox couples.

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Conflicts of interests

Author declares that there is no conflict of interest.

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